Chemical types of bounding of natural radionuclides in TENORM

(*Technologically Enhanced Naturally Occurring Radioactive Materials*)

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Summary

The investigation of the TENORM samples for their initial activity concentrations, the chemical types of bounding the contained natural radionuclides occur, the resulting radon emanation coefficients and finally the transfer factors, leads to the following statements:

- **Phosphate industry:**
  1. In dependence from the geological origin, the used raw materials and the produced fertiliser can contain enhanced initial activity concentrations, the latter mainly uranium
  2. From the raw materials ^{226}Ra can be easily mobilised, in case of the phosphogypsum waste and produced fertiliser attention must be paid for ^{238}U and ^{210}Pb
  3. Highly contaminated raw materials can result in enhanced radon emanation rates, also the fertiliser can contribute to some radon enhancement
  4. There is a well developed transfer factor for ^{226}Ra from all materials involved into plants

- **Aluminium industry:**
  1. In dependence from the geological origin, the used raw materials can contain enhanced initial activity concentrations
  2. ^{226}Ra is the relevant radionuclide and can be easily mobilised from the raw materials and the waste as well
  3. Highly contaminated raw materials can result in strongly enhanced radon emanation rates,
  4. Transfer factors are established for ^{226}Ra into water from both types of bauxites

- **Refractory industry:**
  1. Enhanced initial activity concentrations occur in the additive zircon sand and the fused zirconia mullite products
  2. ^{226}Ra is the relevant radionuclide being present in all materials but not really leachable, ^{210}Pb can be easily mobilised from the filter dust waste in some extent
  3. The radon emanation rates are generally low
  4. ^{228}Th is transferable into water and plants

- **Crude oil exploitation:**
  1. Enhanced initial activity concentrations especially of ^{210}Pb occur in the sludge and scale wastes
  2. ^{210}Pb is the relevant radionuclide being present in all materials and is mostly bound to organo-sulphur compounds, relatively few amounts are easily mobilisable
  3. The sludge can cause really high radon emanation rates
  4. The sludge releases both radium isotopes and ^{228}Th as well for water

- **Hard coal extraction:**
  1. Enhanced initial activity concentrations of ^{226}Ra can occur close to the mining water discharge point and along the riverbanks

2. ^{226}Ra is the relevant radionuclide being enhanced present in all materials, but is not mobilisable, ^{228}Th is found under easily available, reducible and oxidisable conditions

- **Thorium compounds industry:**
  1. Strongly enhanced initial activity concentrations of ^{228}Ra and ^{228}Th can occur in soils being influenced by former thorium processing
  2. ^{228}Ra and ^{228}Th are proven to be available especially for plants
  3. The resulting transfer factors for the pathway "solid-plant" concern all radionuclides

- **Uranium industry:**
  1. Strongly enhanced initial activity concentrations occur in the uranium ores and the tailing wastes, unwanted by-products can be contaminated partly
  2. All uranium radionuclides are not preferably bound in the raw materials, especially ^{226}Ra and ^{210}Pb can be easily leached from the tailings, the unwanted by-products dead rocks mainly contain the uranium radionuclides bound to sulphides, sediments show uranium radionuclides being bound to oxides, the most of them is strongly fixed
  3. The uranium ores and tailing wastes cause really high radon emanation rates, in case of dead rocks they are lower, contaminated sediments can show enhanced emanation rates
  4. Important transfer factors are set from tailings into water for ^{226}Ra and into plants for uranium and lead, from sediments ^{226}Ra can be transferred into plants

- **Investigation procedure:**
  1. The developed investigation procedure as presented in this study to determine simultaneously many radionuclides in extraction liquids by gamma-spectrometry is more applicable and reliable for highly contaminated samples
  2. The influence of different grain sizes on the radionuclides' mobilisation potential is rather low
  3. Uranium oxides can not be cracked by scientific extraction procedures
  4. Some limitation of the investigation procedure seems to be given by the low amounts of starting material for the extraction procedures as proposed in their instructions and the resulting small extraction liquid volumes

For all those reasons, TENORM must be controlled not only for their initial activity concentrations, radon releases and the resulting radiological hazard, but for their radionuclide mobilisation potential and environmental influences, too.

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1 Introduction

The contamination of certain solid materials used in frame of industrial production processes by natural radionuclides was firstly discovered in the beginning of the last century in wastes from crude oil exploitation (ELSTER & GEITEL, 1904). Since then, some more types of industries have been identified dealing with materials containing enhanced levels of natural radionuclides, which are summarised as TENORM (***T***echnologically ***E***nhanced ***N***aturally ***O***ccurring ***R***adioactive ***M***aterials). Radiation protection agencies and the industries as well became aware of the radiological risks for employees and sometimes also for members of the public. Therefore, some efforts were undertaken by national (German Federal Agency for Radiation Protection, BfS) and international authorities (European Commission, EC) to characterise the relevant production processes and the occurring radiological hazard dimensions and to establish limits initiating intervention actions for reducing the radiation risk.

From November 2001 until March 2005, the EU-project "New approach to assessment and reduction of health risk and environmental impact originating from TENORM according to requirements of EU directive 96/29" – acronym TENORMHARM – was carried out during the 5th Framework Program of the European Commission. Participants from the CEEC (***C***entral and ***E***astern ***E***uropean ***C***ountries) Czech Republic, Hungary, Poland, Romania and Slovenia, which are now EU-member-states, as well as the EU-countries Germany and Belgium joint that project. The aim of TENORMHARM, which is listed under the contract-number FIGM-CT-2001-00174, was to consolidate and advance European knowledge and competence in radiation protection and this doctoral thesis was partly financed and carried out within the project. Some of the participating authorities provided TENORM samples, which were derived from industries being typical for each of the countries, and additional samples were taken in Germany. The specimens cover raw materials, wastes and products of the following types of industry: fertiliser production, aluminium production, refractory industry, crude oil exploitation, hard coal mining and Th-contaminated soils as well as uranium industry.

Although the magnitudes of initial radionuclide concentrations contained in specific TENORM and in some cases the resulting effective dose coeffcients are well known and published (RP 95, 1999, PENFOLD et al., 1999), the environmental influences caused by leaching of natural radionuclides from TENORM are still unknown. Therefore, the main focus of the presented work is set on the radionuclides' chemical type of bounding, which is accompanied by investigations for characterising the radionuclides' water and plant availability. The total objectives of this thesis can be summarised as follows:

1. measurement of the initial activity concentrations contained in TENORM
2. determination of the radionuclides' chemical type of bounding
3. identification of radionuclide transfers within a processing scheme
4. determination of the radiological hazard potential caused by emanating radon
5. estimating transfer factors for the pathways "solid-water" and "solid-plant" for each type of industry

The radionuclides of interest are ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th. In order to verify their chemical types of bounding, three different extraction procedures are applied leading to five significant fractions, which are determined for their radionuclide content. By relating the latter to the initial radionuclide content, the radionuclide's leachable portion under specific chemical conditions can be assessed. For this purpose, a new measuring calibration was introduced and adapted.

On the basis of the determined initial activity concentrations, transfer models are developed so migration pathways and hot spots of the radionuclides within an industrial processing scheme can be identified. Since radon can contribute to the effective dose by inhalation due to its volatile character, the solid materials are also investigated for their radon emanation coefficients. By doing so, an estimation of this additional hazard potential is enabled. Finally, the extracted radionuclide concentrations leached by the German DIN extraction procedures are rated and used by defining transfer factors for the pathways "solid-water" and "solid-plant" according to each type of industry.

The described analysing procedures provide information about potential migration pathways of the natural radionuclides stored in TENORM as well as radiological risks for employees dealing with TENORM and members of the public possibly affected, e.g. by dump-sites.

2 Radioactive materials

2.1 Radioactivity

The chemical behaviour of an element is determined by its electronic configuration (RIEDEL, 1994). In contrast, the phenomenon of radioactivity just depends on the composition of the element's nucleus, which means the balance of neutrons in comparison with the amount of positrons. The nucleus of a radioactive element is unstable in its energy condition and therefore characterised by spontaneously decaying resulting in emitting ionising radiation, which can change the physical or chemical structure of other atoms of matter it passes through. This radiation consists of either alpha or beta particles and is commonly accompanied by simultaneous gamma radiation (STROPPE, 1994). Alpha particles are positive charged helium nuclei and are easily absorbed by a few centimetres of air and are not able to penetrate a sheet of paper or the human skin. Nevertheless, in case of incorporation alpha particles are the most destructive kind of radiation. Beta particles are occurring if there is an oversized amount of neutrons in comparison with the amount of protons and do consist of fast, negatively charged electrons, so another positron is created in the nucleus. Beta particles can affect in metre-scale in air; in case of soft tissue they reach a few millimetres up to centimetre. Gamma radiation is a type of high energy electromagnetic wave and therefore consists of photons, whose energy in each special case depends on the kind of nucleus decaying, the kind of conversion happening and the stability of the next produced nucleus. It occurs if in the process of disintegration an unstable nucleus is created, which then transforms into basic conditions by emitting photons. Gamma ray is the most penetrating kind of ionising radiation without a specific elimination distance, which therefore means weighty materials of high atomic numbers, e.g. lead (Z=82), must be used as a protection shield for weakening (BORSCH et al., 1996).

Radioactive elements can either occur as natural ones or being man-made as artificial ones. The last are mainly due to nuclear energy production or nuclear weapon development. Radioactive elements are also called radionuclides and can be concentrated in solid or liquid materials, in case of radon and its isotope thoron also as volatiles in tight spaces by either natural or human factors.

Natural radionuclides are separated into cosmogenic and primordial ones. The cosmogenic natural radionuclides are continuously created by interactions of cosmic radiation in the atmosphere (e.g. ^{3}H or ^{14}C), whereas the primordial natural radionuclides are still present since the act of nucleosynthesis before the planet earth was formed due to their rather long half-lives. The resulting progenies are defined as radiogenic and can be distinguished into those being part of a decay series and those of just one disintegration process resulting in a stable nucleus immediately (e.g. ^{40}K decaying into ^{40}Ar). There are existing three disintegration schemes classified by the initial decaying radionuclide: ^{238}U, ^{232}Th and ^{235}U (fig. 2-1). Each of them results in a stable lead isotope after passing more than a decade of disintegration steps of other elements and their isotopes.

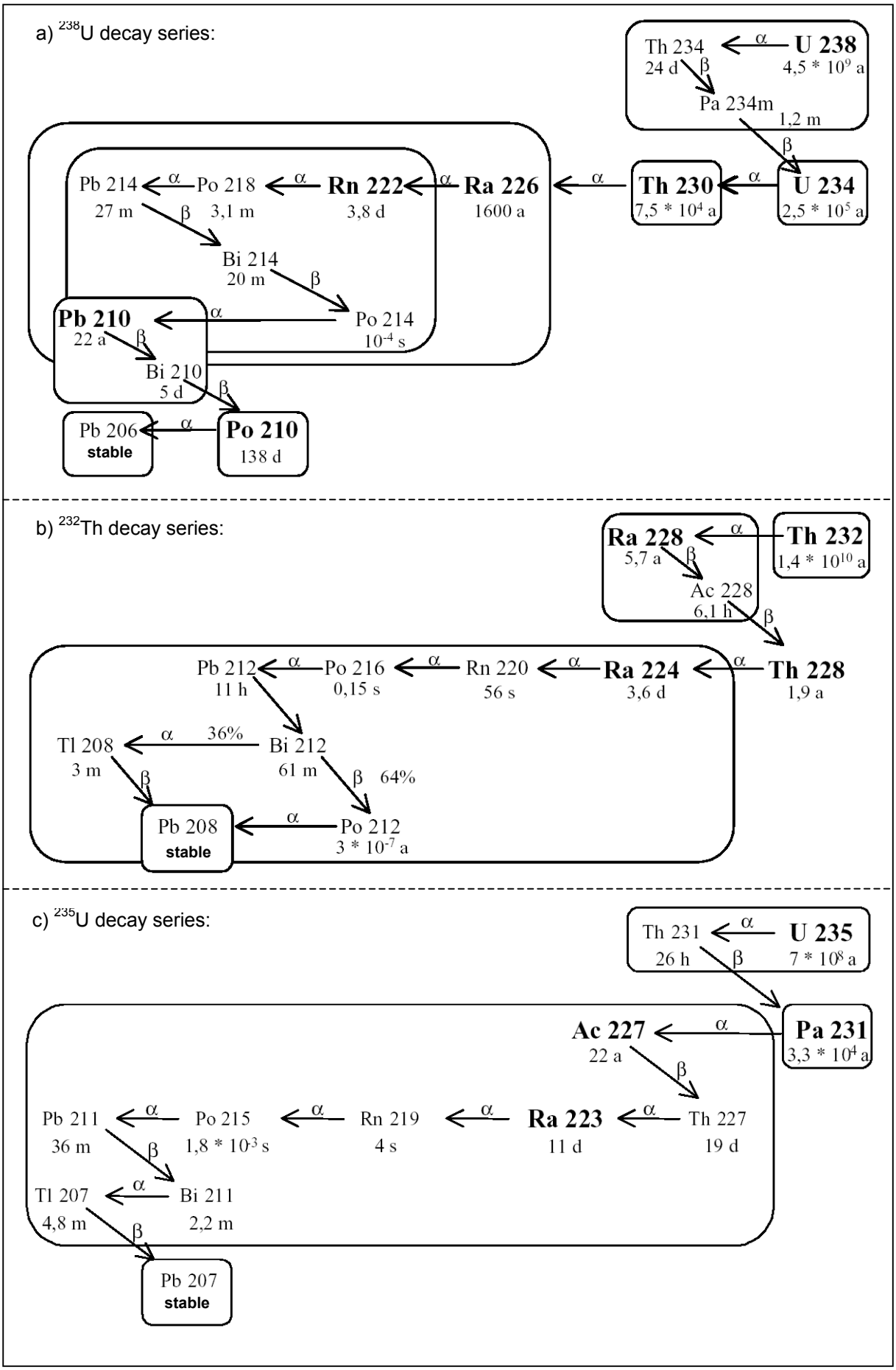

Fig. 2-1: The three natural decay series classified by the first decaying radionuclide (based on SURBECK, 1995, and SCHMIDT, 2001).

2.2 Definitions of radioactive materials

In general, there do exist some different acronyms concerning natural radioactive materials which were introduced by special intentions during time. NORM is most commonly used and comprises all solid ***N***aturally ***O***ccurring ***R***adioactive ***M***aterials being created by natural processes. Rarely, the term NOR is also used for the same meaning (VANDENHOVE, 2002), but in fact it is slightly different because it stands for ***N***aturally ***O***ccurring ***R***adionuclides and therefore just being focused on the radioactive elements and not on the materials the radionuclides are stored in (KNAEPEN et al., 1995). The following simplified scenario gives an example of how NORM can be created and can occur. In frame of the geological genesis called magmatic differentiation uranium/thorium (if present) are relatively enriched in the magmatic fluid because they are incompatible elements due to their ion radius. Therefore, uranium and thorium are then fixed in the crystal lattice of late solidified minerals such as the heavy minerals zirconium or monazite (DYBEK, 1962). Those accessory minerals can show uranium and thorium concentrations of some thousands Bq/kg. In further consequences, the rock types containing those accessory minerals can also show high radionuclide concentrations. If uranium was not enabled to crystallise in those minerals during magmatic differentiation, then it might be forced by decreasing temperatures and pressures to get solidified by oxidation as black spheroid pitchblende e.g. along cracks and grain boundaries in rocks, today maybe outcropping close to the surface. This kind of accumulation mainly occurs in case of silicate rocks (granite or pegmatite) being made of common and frequent minerals (KEMSKI et al., 1996). Granites exposed to weathering processes may provide the uranium for erosion transports, which further on may lead to an enhanced concentration of heavy minerals in placers along riverbanks or onshore called mineral sands.

NARM is dealing with natural radioactive materials, too, but in addition also with those being artificially produced during the operation of atomic particle accelerators. The latter occur in frame of medical appliance (radionuclide is injected into a patient and in therapeutic applications for eliminating cancerous tumours), research work (used in University teaching programs in such fields as physics, biology and medicine) or industrial processing (incorporated as an integral part of gauges which are used as level indicators and measuring devices) and the acronym means ***N***aturally Occurring or ***A***ccelerator Produced ***R***adioactive ***M***aterials (BRADLEY, 2003).

All these acronyms mentioned above concern radioactive materials showing radionuclide concentrations made by natural phenomenon, in case of NARM including artificial accelerators. If the radionuclide content of natural radioactive materials is unintended enhanced by man-made procedures, the acronym TENORM is widely used meaning ***T***echnologically ***E***nhanced ***N***aturally ***O***ccurring ***R***adioactive ***M***aterials for emphasizing the technical factor. Notwithstanding, the terms TENR or ENOR can also be found for the intentions of ***T***echnologically ***E***nhanced ***N***atural ***R***adioactivity (EDMONSON et al., 1998) respectively ***E***nhanced ***N***aturally ***O***ccurring ***R***adioactivity. In 2002, PASCHOA & GODOY picked up once again the acronym HINAR to determine areas affected by ***HI***gh ***NA***tural ***R***adioactivity, which has been used initially in 1975 within the title of the first international conference dealing with both, NORM and TENORM, held in Brazil.

According to the example for NORM given above, the term is used to describe natural materials such as mineral sands. These placers may exceed background radionuclide concentrations, but they are of natural state. If the human component is interacting by treating the mineral sands resulting in separated materials also of higher radionuclide concentrations than the background, these materials are TENORM. According to EPA (2000), in the past some confusion was created by using the acronym NORM simultaneously for the intention of TENORM, especially before 1998. At the NORM IV conference held in May 2004 in Polish Szczyrk, the simultaneous use of all those different acronyms mentioned above was an important part of the round table discussion. The participants came to the conclusion that despite it is not technically the most accurate term, NORM is the most general and commonly used one (IAEA, 2005). In this study, TENORM is used further on because from the scientific point of view it is correct for the presented materials.

One acronym just concerning artificial radionuclides must be highlighted, too, because it also includes the scenario of disposing ***L***ow ***L***evel ***R***adioactive ***W***aste (LLRW) in the environment and therefore of increasing the radiation exposure to members of the public. Beside high and medium level radioactive waste, these ***S***ubstances ***o***f ***L***ow ***A***ctivity (SoLA) are generated by using electricity generation, propulsion units or nuclear weapons resulting in large amounts of radioactively contaminated materials like concrete, glass and metals. As it is reported by the European Committee on Radiation Risk (ECRR, 2003), a non-specified ***E***xemption ***O***rder of 400Bq/kg is fixed as the SoLA EO.

2.3 Categorisation of TENORM

All natural solid substances, which are produced or occur in the environment as a result of human activities and may cause enhanced exposure to both, workers and members of the public, are called TENORM. The enhancement factors can be due to manufacture processes, mining activities and/or water treatment. Therefore, TENORM are characterised by an artificial enrichment or translocation of natural radionuclides and it is out of interest if the factories are still active or were abandoned in the past. A translocation is only considered as a TENORM generating process, if the availability of radionuclides is increased. Per definitionem, the enrichment as well as the translocation are due to physical or chemical processes within the human material treatment. TENORM are accountable for an enhanced radiation against the background in their neighbourhood (LEOPOLD & WIEGAND, 2002).

According to the definition being fixed in frame of TENORMHARM, the primordial radionuclides of the ^{238}U- and ^{232}Th-decay-series are in the focus whilst ^{40}K turns out of any consideration due to its omnipresence. Since it is not workable to use gamma dose rates for identifying TENORM because the measurements are not able to distinguish between individual radionuclides (e.g. between those ones of natural background and of technologically enhanced) and the radiation exposure is strongly connected to the duration of stay, the "activity concentration" given in the SI-unit [Bq/kg] related to dry mass for each radionuclide is used. A material is to be considered as TENORM if just one radionuclide of the ^{238}U or ^{232}Th decay series is exceeding the threshold of **200Bq/kg dry mass**. This limit is in accordance to the

German Radiation Protection Ordinance (StrSchV, 2001) and was also agreed by participants to use in frame of TENORMHARM. It is justified by the correlation of the ambient gamma dose rate of 1mSv/a measured 1m above the ground and the corresponding radionuclide concentration of 200Bq/kg homogenously distributed in the ground.

2.3.1 Types of industries concerned

The knowledge about the phenomenon of enhanced natural radionuclide concentrations in certain materials being part of industrial activities traces back to the early beginning of the 20th century when ELSTER & GEITEL (1904) discovered an enrichment of radioactive substances in thermal brines, which were raised to the surface as an unwanted by-product in frame of oil- and gas exploitation. It was the same year when radon was found in petroleum by HIMSTEDT. Nevertheless, no profound investigations were undertaken until the early seventies. In 1975, GESELL measured elevated ambient gamma dose rates up to 80μSv/h on the installation surfaces of a gas processing plant, which he attributed to radon progenies, and identified ^{210}Pb on the internal surface of processing equipment as a significant potential exposure hazard in frame of maintenance operations as well. In 1965 enhanced gamma radiation was discovered in Polish hard coal mines by SALDAN, but regular surveys have not been started before the seventies by TOMZA & LEBECKA (1981), who determined radium as the main radiation cause due to the pumping of radium-bearing waters from the underground to the surface. In 1982 also GANS et al. reported the occurrence of high radium concentrations in waste waters from hard coal mining in the German Ruhr-basin. During time some more substances of other industry types were found to contain enhanced levels of natural radionuclides, too, and in 1959 the World Health Organisation (WHO) published a report regarding the genetic effects which might be produced in humans due to the increasing use of ionising radiation in medicine, science and industry (WHO, 1959). In 1975 the first international conference dealing with TENORM (at that time called HINAR) was held in Pocos de Caldas, Brazil (CULLEN & PENNA FRANCA, 1977). Nowadays, international conferences are held continuously in periods of some years such as the TENR- or NORM-conferences. The progressing investigations of those radioactive materials resulted finally in the identification of different industry types as being of potential radiological relevance. Especially in North America as well as in the EU catalogues of affected industries have been published, the most representatives are:

- "EPA's guideline for Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM)" of the US Environmental Protection Agency (EPA) [2000]
- "Canadian guidelines for the management of naturally occurring radioactive materials (NORM)" of the Canadian Federal Provincial Territorial Radiation Protection Committee (CRPC) [2000]
- "Materials containing natural radionuclides in enhanced concentrations" of the European Commission [EUR 17625, 1997]
- "Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally-occurring radionuclides" of the European Commission [Radiation Protection 107, 1999]

The Canadian Radiation Protection Committee (CRPC, 2000) proposed a rough classification system for TENORM-industries to be summarised in six groups, which is taken as the basis for the following categorisation:

1. Metal ore processing and metal recycling

Enhanced natural radionuclide concentrations may occur when metal ores are mined or processed. Beside the ores themselves generated sludge and scales are the main contaminated materials. The possibility of redistribution as scrap metals to other industries resulting in the formation of new contaminated products must be taken into account, too. The following types of industries are concerned:

a. Tin
b. Niobium
c. Aluminium
d. Iron and steel
e. Zinc
f. Copper
g. Molybdenum
h. Vanadium
i. Hafnium
j. Lead

2. Mineral extraction and processing

Enhanced natural radionuclide concentrations may occur when mineral sands/ores are mined or processed. Beside the sands and ores themselves phosphogypsum, tailings and sludge are the main materials. The following types of industries are concerned:

a. Fertiliser industry
b. Abrasive and refractory industries
c. Rare earth element industry
d. Thorium compound industry
e. Titanium dioxide pigment industry
f. Uranium mining

3. Organic material processing

Enhanced natural radionuclide concentrations may occur when crude oil or natural gas is pumped to the surface. Scales in technical installations as well as sludge are the most important materials. The following types of industries are concerned:

a. Oil and gas extraction
b. Hard coal mining

4. Thermal-electric production

Enhanced natural radionuclide concentrations may occur when hard coal is combusted, which leads to contaminated ashes remaining in the combustion vessels. The following industry type is concerned:

a. Hard coal power plants

5. Water treatment facilities

Enhanced natural radionuclide concentrations may occur when fresh or waste water is treated by adsorptive media or ion-exchange resins to remove minerals and other impurities from the water. In case of drinking water and geothermal productions the radionuclide concentration strongly depends on the geological formation the groundwater is extracted from. Sludge is the main material. The following types of industries are concerned:

a. Waterworks
b. Waste water treatment plants
c. Geothermal installations

6. Tunnelling and underground workings

Enhanced natural radionuclide concentrations may occur in areas where galleries are installed in rocks containing indigenous radioactive minerals or releasing radon/thoron due to their porosity or cracks. According to the definitions given in this study, this group is not part of TENORM but NORM. The following installations are concerned:

a. Underground caverns
b. Underground radon-spas
c. Electrical vaults
d. Tunnels
e. Sewer systems
f. special case: Chinese resident caverns constructed in loess as well as buildings made of loess bricks (GUO et al., 2001)

2.3.2 Types of materials concerned

As it appeared in frame of TENORMHARM, it is also useful to classify the substances containing elevated concentrations of natural radionuclides due to their position in the processing schemes. According to PENFOLD et al. (1999), raw materials can contain activity concentrations of several, even hundreds of Bq/kg of naturally occurring radionuclides, often concentrated by the same natural process that concentrates the elements in which the raw material is rich. Such materials are typically extracted and processed in very large quantities. The physical characteristics may range from a beach sand to a dense rock. It is more common nowadays for such materials to be imported into the EU from developing countries. Their processing may concentrate the radionuclides in unwanted by-products in both, technical installations and in the environment, as well as in residues. This can occur by means of mass separation (e.g. in processing certain mineral sands), other physical phenomena (e.g. the volatilisation of lead and polonium in high temperature furnaces) or by chemical reactions (e.g. the precipitation of radium containing scales in tubes). The activity concentration of by-products or residuals may be high as several thousands Bq/kg of certain radionuclides. The quantities of such material are often smaller than those of raw materials, particularly those by-products with high activity concentrations. Then, in some cases the resulting products intentionally contain high levels of naturally radioactive elements such as thorium, although not for the radioactive properties of the elements. An example of such a use is that of thorium in welding electrodes, where it aids arc ignition and stability. The activity

concentrations of such materials may be quite high, perhaps several thousands of Bq/kg. In summary this gives a total of five groups:

1. **Raw materials**
   e.g. raw phosphate, uranium ore
2. **Unwanted by-products (waste) in technical installations**
   e.g. scales in the oil & gas industry's tubes, sludge in underground galleries and/or tailings in surface settling ponds
3. **Unwanted by-products (waste) in the environment**
   e.g. river bottom sediments, flood plain soils or dead rock stockpiles
4. **Residuals**
   e.g. fly ash, slag
5. **Final and intermediate products**
   e.g. fertilisers, thoriated welding electrodes, alum earth, building materials

Furthermore, industrial processes may also release gaseous natural radionuclides (mainly radon and thoron) to the environment (important example: radon release to indoor air in waterworks) or by shafts into the atmosphere (e.g. hard coal combustion) (MARTIN et al., 1997).

2.4 Pathways and scenarios

In order to establish the significant industries and the techniques for categorising their processes, it is necessary to identify the pathways by which workers could receive a significant radiation dose. Due to the large differences in quantities of materials containing enhanced natural radionuclide concentrations by type of industry, exposure conditions in these industries can differ considerably with respect to industry type, workplace conditions and radionuclides involved (VAN DER STEEN et al., 2004). PENFOLD et al (1999) described five pathways and connected them with situations the workers are most exposed:

1. **Inhalation of dust**
   most exposed situation: in dusty conditions with little respiratory protection
2. **Ingestion of dirt/dust**
   most exposed situation: in dirty and dusty areas with little protective clothing
3. **External irradiation**
   most exposed situation: close to large amounts of material with little shielding
4. **Inhalation of radon**
   most exposed situation: in rooms with large amounts of material and little ventilation
5. **Skin contamination**
   most exposed situation: perhaps by ingestion, but can be mostly neglected

That means due to the predomination of dusty work conditions as a most exposed situation, internal exposure is in many cases the dominant exposure pathway for TENORM. Furthermore, those situations can be separated into a likely (normal) and unlikely version (PENFOLD et al.,

1999). Under normal assumptions parameters are taken which are towards the conservative end of what would be considered to be the normal range (e.g. a typical ventilation rate of 0.5 air changes per hour can be assumed in most factory situations, which is appropriate for a work space with no forced ventilation – in modern workplaces some ventilation is usually installed). In case of unlikely assumptions parameters are taken that are very unlikely to occur, but are still plausible (e.g. the maximum time a worker can spend next to a pipe containing contaminated scale, known to be in a remote area of a plant, is set to several hundreds hours per year). In RP 95 (1999), three different but typical exposure scenarios were presented by considering work activities that may occur with three broad categories of material: stockpiles, residues and material in tanks, vats or tubes. The situations are based on observations of the processes concerned and the possible pathways as presented above are divided into normal and unlikely assumptions:

1. **Stockpiles of materials: exposure of a warehouse operative**
   A worker is exposed to the material whilst working in a warehouse containing a very large quantity of it and where the atmosphere is dusty. The worker spends most of the working period in the warehouse, close to the material, breathing and picking up dust generated from loading and unloading the material.
   a) External exposure:
      A 100 or 1000m^3 unshielded source represents a large stockpile. The worker is assumed to be 1m from the source for 400 hours per year under normal or 2000 hours per year under unlikely assumptions.
   b) Inhalation of dust:
      The worker is assumed to work for 2000 hours per year without respiratory protection in an inhalable dust concentration of 1mg/m^3 under normal and 5mg/m^3 under unlikely assumptions.
   c) Ingestion of dust:
      Over a 2000 hour year, the worker is assumed to ingest inadvertently 1.25mg per hour under normal and 3.75mg per hour under unlikely assumptions.
   d) Inhalation of radon:
      Over a 2000 hour year, the worker is assumed to breathe radon exhaled from the stockpile. The warehouse ventilation rate is taken as 0.5 air changes per hour under normal and 0.25 air changes under unlikely assumptions. The room in which the worker is exposed is assumed to be 4* the material volume or 100m^3, whichever is larger.

2. **Residues and scales: exposure of a worker removing residues**
   The worker is exposed when removing residues, i.e. cleaning tubes or vessels. The worker performs this operation infrequently (perhaps a day a week or an hour a day), but is exposed to high concentrations of dust in the removal process. The exposure is caused by volatilisation of polonium or sometime lead (e.g. in high temperature furnaces), and the collection of radium in tube scales. The quantity of material present is usually between some kilograms and a few tons. Any quantity of residues larger than this could be treated as a stockpile. Some respiratory protection can be assumed in the normal set of assumptions, i.e. protective equipment is more likely to be worn, exposure times are shortened and tubes or vessels can be taken as cleaned before cutting.

a) External exposure:
The worker is assumed to be 1m from an unshielded $1m^3$ the source for 100 hours per year under normal or 400 hours per year under unlikely assumptions.

b) Inhalation of dust:
The worker is assumed to work in a dust concentration of $10mg/m^3$ for 100 hours per year under normal and 400 hours per year under unlikely assumptions. However, use of respiratory protection is assumed to halve the dust loading actually inhaled under normal assumptions.

c) Inhalation of fume:
The worker is assumed to be exposed without respiratory protection to volatilised polonium or lead, equivalent to a dust concentration of $1mg/m^3$, for 100 hours per year under normal and 400 hours per year under unlikely assumptions.

d) Ingestion of dust:
Under normal assumptions, the worker is assumed to ingest inadvertently 5mg/per hour for 100hours per year, but the ingestion rate is halved by the use of protection equipment. Under unlikely assumptions, the exposure period is increased to 400 hours per year and no protective equipment is worn.

e) Inhalation of radon:
Under normal assumptions, the worker is assumed to breathe radon exhaled from the residue for 100 hours per year with a ventilation rate of 0.5 air changes per hour. Under unlikely assumptions, the exposure time is increased to 400 hours per year and the ventilation rate is reduced to 0.25 air changes per hour.

3. Process material in vessels and tubes: exposure of a general worker

Workers are quite likely to be incidentally exposed to radioactive scales that has been built up in tubes and vessels for a significant fraction of their working year. Due to the scale's consistence, the only exposure pathway is by external irradiation and in addition, some shielding from the tube or vessel walls, which are taken to consist of 5mm thick iron, is assumed, too.

a) External exposure:
The worker is assumed to be 1m from a $100m^3$ source for 400 hours per year under normal or 2000 hours per year under unlikely assumptions.

By connecting such pathways and exposure scenarios it is possible to calculate doses received from the material of a defined activity level. Of course, these calculations can then be reversed to lead from a defined dose level to an activity in the input material. This has been done for some important types of industries such as fertiliser production or oil and gas extraction respectively the materials involved and is presented by PENFOLD et al. (1999).

2.5 Classification systems

In order to estimate what radiological hazard dimensions of the respective TENORM type is to be expected and what regulations should be undertaken, a simplified classification of the

category 1 no regulations necessary	max. effective dose (RP 95, 1999) normal unlikely 1mSv/a 6mSv/a	activity concentration of at least one radionuclide of the ^{238}U decay series (SSK, 1992) <200Bq/kg
category 2 lower level of regulation	max. effective dose (RP 95, 1999) normal unlikely 6mSv/a 20mSv/a	activity concentration of at least one radionuclide of the ^{238}U decay series (SSK, 1992) >200Bq/kg
category 3 higher level of regulation	max. effective dose (RP 95, 1999) normal unlikely 20mSv/a 50mSv/a	activity concentration of at least one radionuclide of the ^{238}U decay series (SSK, 1992) >1000Bq/kg
category 4 process not permitted	max. effective dose (RP 95, 1999) normal unlikely >20mSv/a >50mSv/a	

Figure 2-2: Classification system based on annual effective doses proposed by the European Commission (RP 95, 1999) and activity concentrations related by the German Commission on Radiation Protection for residual areas affected by uranium mining in the former GDR (SSK, 1992).

materials is needed. As mentioned in chapter "2.3 Categorisation of TENORM" there is a rough correlation between activity concentration and effective dose received, which is calculated in detail for some special types of material by PENFOLD et al. (1999). Therefore, it is possible to generate a relationship between the activity concentrations and the effective doses a human receives under well defined conditions. Since each radionuclide causes individual harm dimensions due to its physical disintegration properties, there is no general and exact classification system providing a clear link between the radionuclides' activity concentrations, effective doses received and the degree of regulations needed. In RP 95 (1999), a scheme is proposed concerning general limits of effective doses, which has been additionally related to activity concentrations of radionuclides being part of the ^{238}U decay series by the German Commission on Radiation Protection (Strahlenschutzkommission SSK) (SSK, 1992). The latter was established to enable measurements of an easy but also reliable parameter which is able to distinguish between natural background and technologically caused radiation exposure. This distinction was important in frame of surveys on residual areas affected by the extensive uranium mining in the former German Democratic Republic (GDR). The effective dose marker point defined in RP 95 (1999) when no actions are necessary is fixed at 1mSv/a under normal assumptions (6mSv/a under unlikely assumptions) and that is the same to which the system of activity concentrations proposed by the German Commission on Radiation Protection is referred

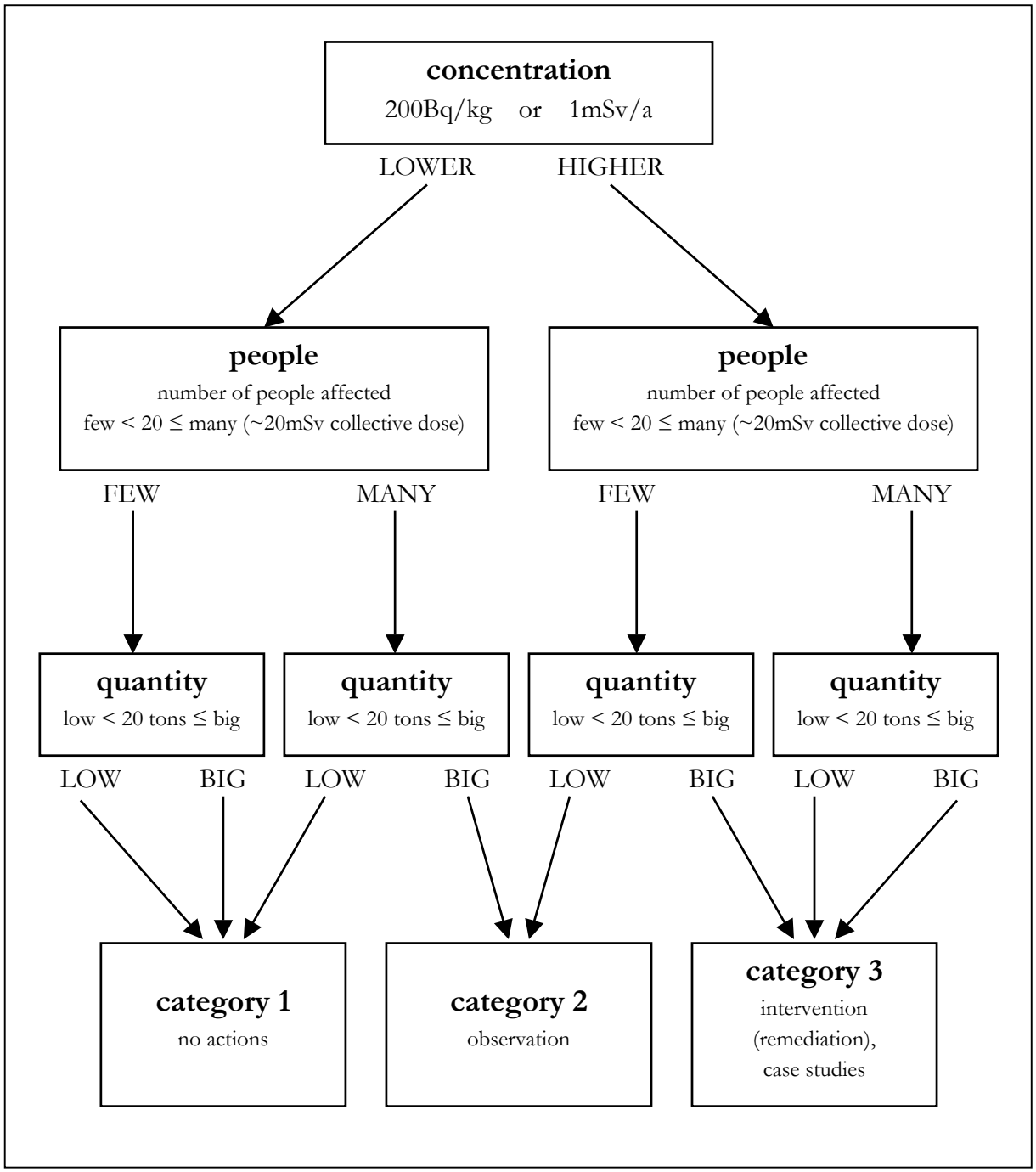

Figure 2-3: Classification system according to activity concentration/effective dose, number of people affected and quantity of material resulting from processing (MICHALIK, 2005).

to. Therefore, both systems are presented in a comparing style (fig. 2-2). In frame of TENORMHARM, a further classification system was developed also taking into account the number of persons affected (workers and members of the public) respectively their collective dose as well as the quantity of material resulting from processing (fig. 2-3). It is also referred to a threshold of 1mSv/a effective dose respectively 200Bq/kg for at least one natural radionuclide and leads to three categories comparable to those shown in fig 1: category 1 means no actions are necessary, category 2 demands for observation and the last category says intervention actions must be carried out (MICHALIK, 2005).

2.6 Legislative aspects

The legislative situations in EU member states concerning TENORM differ widely in some cases. In fact there are still differences in the identification progress of workplaces which could be affected by enhanced ionising radiation among the initial 12 EU member states, i.e. in Denmark, Greece and Spain this process is going on whilst in Portugal no actions are undertaken until now, the other 8 countries have finished it (POFFIJN & WEISS, 2005). Therefore, one of the aims of TENORMHARM was focused on the examination of relevant national regulations in the participating countries to identify common features and differences between them respectively to promote activities towards harmonisation of legislation. On 13th May 1996, the European Council has adopted the EU COUNCIL DIRECTIVE 96/29/EURATOM, which lays down "Basic Safety Standards (BSS) for the protection of the health of workers and the general public against the dangers arising from ionising radiation". Its Title VII deals with the "significant increase in exposure due to natural radiation sources" and therefore includes the main radiation protection issues related to NORM and TENORM. The Directive is addressed to the member states and must be implemented into national legislation, for assistance to Title VII a technical guidance was established under Article 31 of the EURATOM Treaty and published as RP 88 (1997). That means EU member states are obliged to identify the work activities that can not be ignored from a radiological protection point of view and declare parts of the Directive applicable in their national regulations with respect to natural sources. Nevertheless, there is still a need for more practical guidance, both for the operator and for the regulator, on appropriate control measures and the extent to which these can be achieved (VAN DER STEEN et al., 2004).

In Germany, the private company *Brenk Systemplanung* was engaged in 1999 to identify workplaces may be affected by elevated ionising radiation and to summarise quantities of occurring materials respectively their radionuclide activity concentrations contained (BARTHEL et al., 2000). In frame of the revision of the Radiation Protection Ordinance, the chapter concerning NORM/TENORM was based on the proposals mentioned in that report. The revised Radiation Protection Ordinance fulfils the demand for implementing the EU COUNCIL DIRECTIVES 97/43/EURATOM "Health protection of persons against hazards resulting from ionising radiation occurring as medical exposition" as well as 96/29/EURATOM into German legislation. It was published in 2001 as Federal Statute No. 38 and comprises five parts (STRSCHV, 2001):

Part 1: General instructions
Part 2: Protection of person and environment against radioactive materials or ionising radiation occurring in frame of special activities
Part 3: Protection of person and environment against natural radiation of occupation
Part 4: Protection of the consumer on addition of radioactive substances in products
Part 5: Common instructions

That means in consequence, there is a distinction between "radiation caused by intention – artificial" (part 2) and "natural radiation" (part 3). TENORM are treated in §97 within part 3 as "residuals to be supervised", which are then defined in detail in annex XII part A. The lower activity concentration threshold is set to 200Bq/kg for each radionuclide of the ^{238}U and ^{232}Th decay series.

3 Investigated industrial processes producing TENORM

Almost at all half-year meetings during the progress of TENORMHARM, which each time took place in another participating country, solid samples were taken at sites where relevant TENORM occur in that special country. In addition, samples were collected in Germany at a site having been contaminated by thorium and at another being influenced by hard coal mining. Samples were also provided by a German oil and gas extraction company and an refractory producing company as well. The locations of all sites respectively the affected industry type are shown in figure 3-1.

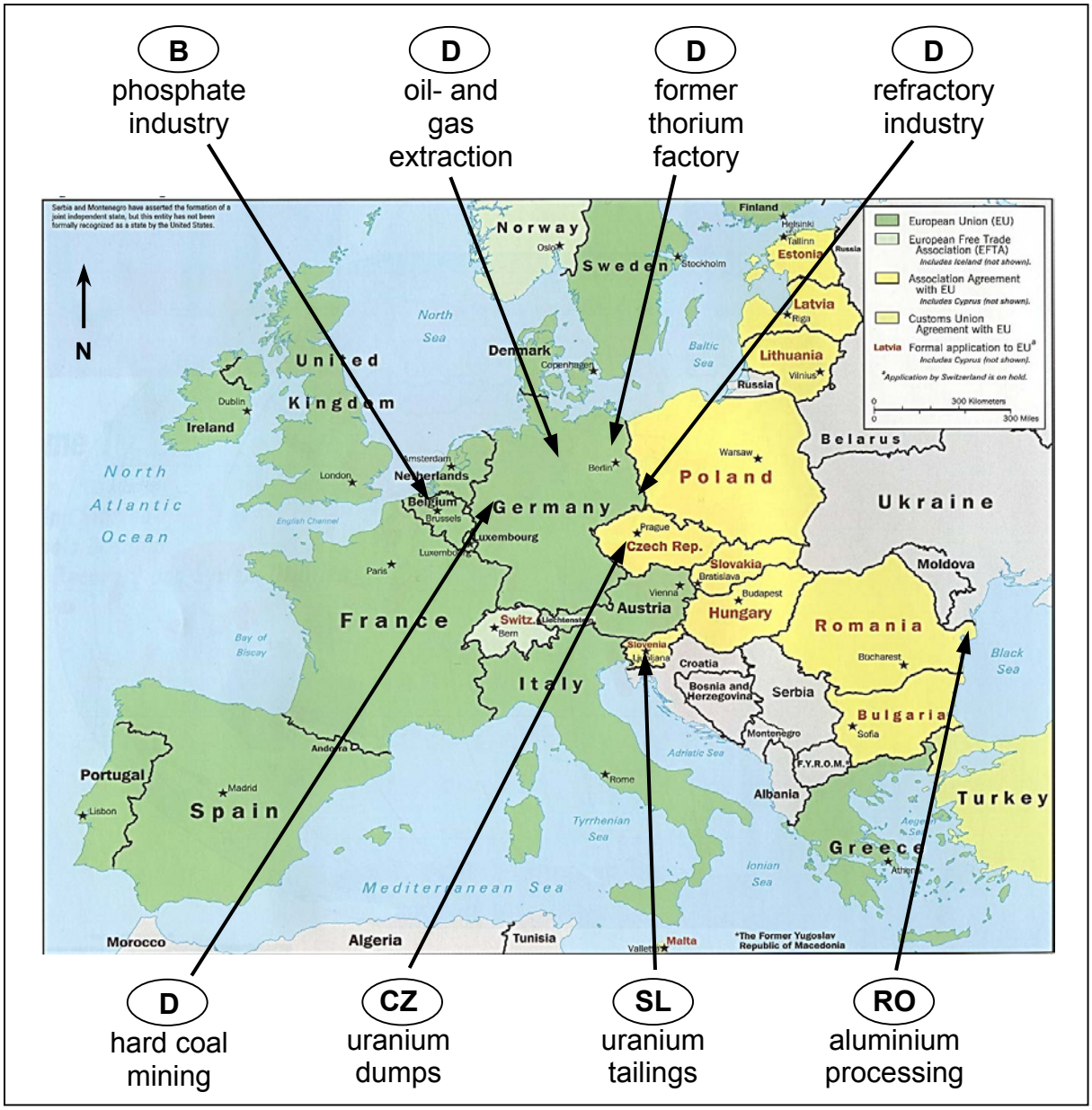

Fig. 3-1: Sample collection locations in Europe (map taken from http://europa.eu.int/eracareers/images/europamap3.gif).

3.1 Phosphate industry

The phosphate rock is the starting material for the production of all phosphate products and is the main phosphorus source for fertilisers (PENFOLD et al., 1999). The composition of phosphate rock depends on the place of its geological origin. Phosphate rock mainly consists of calcium phosphates called apatites, mainly fluorapatites, and can be broadly divided into two classes – sedimentary phosphate rocks and igneous phosphate rocks. The world production mix is almost 7/8 sedimentary rocks and about 1/8 igneous rock (VAN KAUWENBERGH, 1997).

In this study, the focus is set to the fertiliser production. Mineral fertilisers are made from naturally occurring raw materials containing nutrients which have been transformed into a more plant-available form by industrial processing. Although the number of chemical processes used is relatively small, there is a wide variety of finished products. This diversity facilitates site-specific application which takes into account factors such as soil type, the requirements of the crop and weather conditions as well (EFMA, 1997).

All fertilisers contain at least one major plant nutrient. The term "straight fertilisers" is used in connection with fertilisers which have a declarable content of only one of the major plant nutrients, namely nitrogen, phosphorus or potassium. Based on their contents of nitrogen, phosphorus and potassium, fertilisers can be categorised as follows (EFMA, 1997):

1. **Nitrogen fertilisers**
   The only major nutrient these fertilisers contain is nitrogen. The nitrogen used in the production of fertilisers is captured from the atmosphere in a process which uses a catalytic reaction to synthesise ammonia.
2. **Phosphate fertilisers**
   The raw material required for the production of phosphate fertilisers is rock phosphate, no matter which type (igneous or sedimentary). The phosphorus contained in the ore is not, however, readily available to the plants, and is normally processed first.
3. **Potash fertilisers**
   Like phosphate fertilisers, potash fertilisers are mainly derived from geological deposits. The low-grade, unrefined salts obtained from mining could be applied direct, but are normally refined to achieve a more concentrated product. The most commonly used product is potassium chloride, otherwise known as muriate of potash (MOP), which contains 40% to 60% K_2O. For plants which are particularly sensitive to chlorine such as tobacco, potatoes, fruits or vegetables, potassium sulphate, which contains 50% K_2O and 18% sulphur, is used. For use on Mg-deficient soils, potassium magnesium sulphate containing 30% K_2O, 10% magnesium oxide (MgO) and 18% sulphur (S) is used.
4. **Multi-Nutrient (MN) fertilisers**
   Fertilisers containing more than one of the primary nutrients nitrogen, phosphorus or potassium are known as multi-nutrient (MN) fertilisers. They are classified by three different types:
   - complex fertilisers: these contain at least two of the nutrients nitrogen, phosphorus or potassium and are obtained by chemical reaction. The resulting granules therefore contain

the declared ratio of nutrients. The majority of multi-nutrient fertilisers applied in the EU are complex fertilisers.

- compound fertilisers: these contain at least two of the nutrients nitrogen, phosphorus or potassium and are obtained by chemical reaction, by blending or by both. The granules produced may contain the different nutrients in varying ratios.
- blended fertilisers: these are obtained by the dry mixing of several materials. No chemical reaction is involved.

According to EFMA (1997), fertilisers are classified due to the ratio of their nutrient content, in the order N, P (replacing P_2O_5) and K (replacing K_2O). Given the range of soils and crops in the EU, a wide variety of grades is offered to meet the different agronomic and environmental requirements, in some cases substantial quantities of di-ammonium phosphate (DAP) are used, too.

3.1.1 Wet process

There are two production processes applied for phosphate rocks: the so-called "wet process" produces fertilisers whereas the "thermal process" leads to elemental phosphorus to be further used for high grade phosphoric acid and detergents. This study focuses on the fertiliser production and therefore on the wet process, for which the phosphate rock is required to contain phosphorus in the range between 29-39% (RADULESCU & POPESCU, 2002a). Apart from the initial phosphate rock the following substances are involved: ammonia (NH_3), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), potash salts, ammonium sulphate, ammonium phosphates, magnesium salts, dolomite, boron compounds, zinc sulphate, talcum and coating agents as additives.

The investigations presented in this study were carried out on MN-fertilisers, for which the starting material is single-superphosphate (SSP) that is directly produced from the initial phosphate rock. According to WIESENBERGER (2002), SSP is manufactured by treating the phosphate rock with sulphuric acid. Figure 3-2a presents a simplified block flow diagram of the production of SSP in a so-called den. In order to enable the reaction with sulphuric acid, the phosphate rock is firstly ground in a mill and then fed into a mixer, where the phosphate rock is mixed with sulphuric acid (concentration of about 75%) at the required rate. The reaction between sulphuric acid and the fluorapatites contained in the phosphate rock proceeds in two stages. At first, the insoluble phosphate rock is converted into soluble phosphoric acid leading to the wastes of solid calcium sulphate (phosphogypsum), which is produced in dimensions of 5 tons per ton phosphoric acid and usually dumped close by the processing plant, and volatile HF:

$$Ca_5F(PO_4)_3 + 5\ H_2SO_4 \rightarrow 3\ H_3PO_4 + 5\ CaSO_4 + HF \qquad \text{[equ. 1]}$$

The second step is to mix the phosphate rock with the produced phosphoric acid, which then leads to SSP and once again HF as waste:

$$Ca_5F(PO_4)_3 + 7\ H_3PO_4 \rightarrow 5\ Ca(H_2PO_4)_2 + HF \qquad \text{[equ. 2]}$$

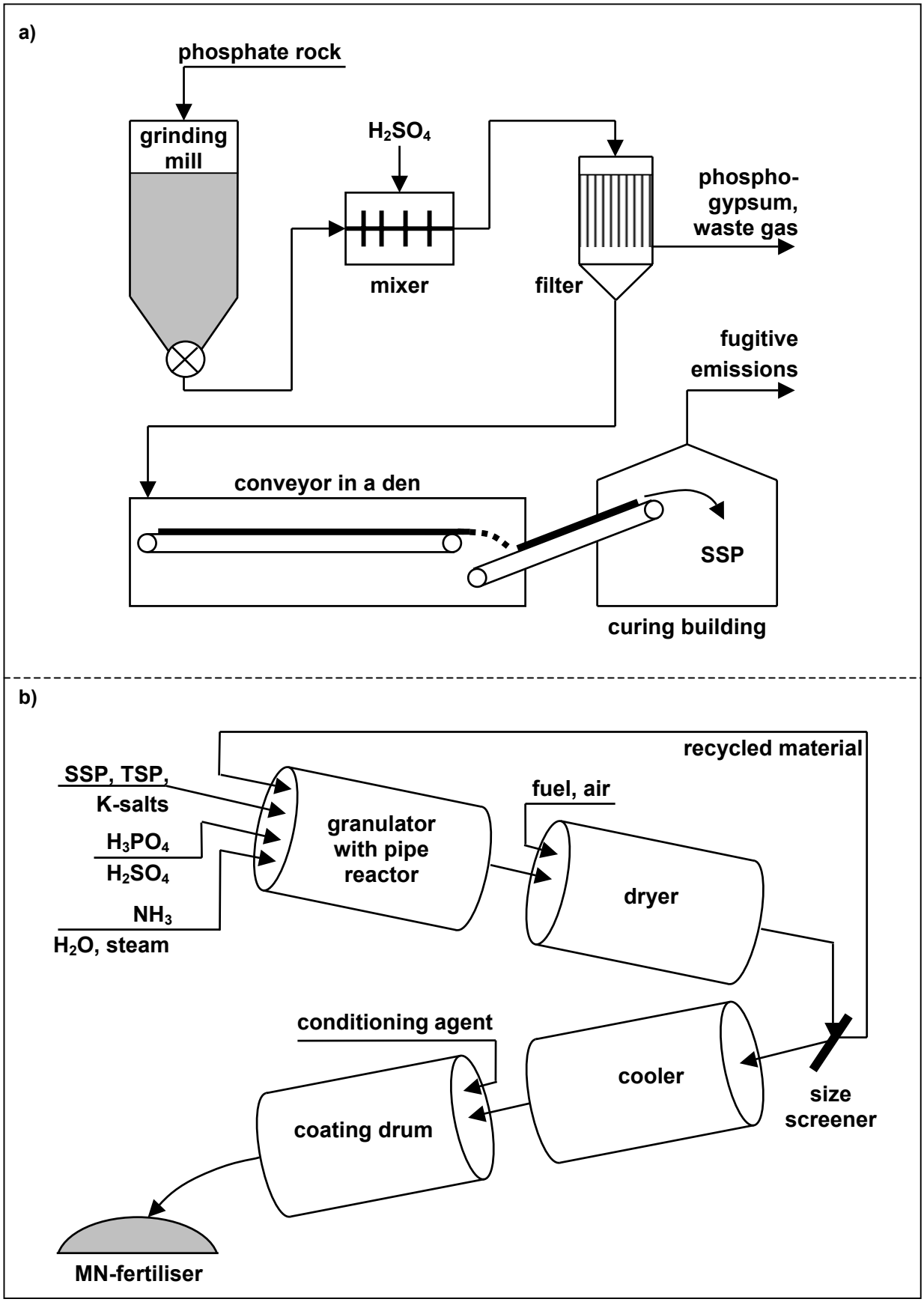

Figure 3-2: Block flow diagram of the fertiliser production by wet process: a) production of single superphosphate [SSP]; b) Multi-Nutrient [MN] fertiliser production [TSP: triple superphosphate] (based on WIESENBERGER, 2002).

After a mixing time of 1-3 minutes, the reaction mass is discharged from the mixer onto a continuously moving enclosed conveyor in a den, which has a slow moving circulating floor. The mass is held in the enclosed area for a residence time of about 20-40 minutes to enable solidification, thereby moving to the end of the den. The solidified mass is then broken up by a cutter and transferred via an enclosed conveyer to a storage pile for "curing" at least for 1 week in order to complete the reaction. Waste gases containing dust and considerable amounts of HF and SiF_4 arise from the digestion of phosphate rock in sulphuric acid. Those waste gases are treated by wet scrubbing, from which waste water emissions arise (WIESENBERGER, 2002).

For the production of MN-fertiliser, also triple-superphosphate (TSP) is needed as an additive. It is manufactured in a very similar way as SSP (equ. 2), but the mixing time of phosphate rock and phosphoric acid is shorter. The heat of reaction is one-third of that for SSP and the same temperature (80-100°C) is reached, but less SiF_4 is evolved. In frame of the MN-fertiliser production, different starting materials are involved depending on the type of fertiliser to be produced:

- phosphoric or sulphuric acid
- SSP, TSP or ammonia or potassium salts
- water, steam

Figure 3-2b presents a simplified block flow diagram of the MN-fertiliser production process. Solid starting materials (SSP/TSP and K-salts) are dosed into a rotary granulation drum, which is combined with a pipe reactor. For the production of NPK-fertilisers ammonia, phosphoric acid or sulphuric acid is dosed via the pipe reactor into the granulation drum. For the production of PK-fertilisers SSP or TSP is granulated together with potassium salts. In the rotary granulation drum the mixture of recycles and raw materials is adjusted for agglomeration by injecting steam and water. The amount of steam and water required for the granulation depends on the formulation of the product and on the temperature in the granulation drum, the resulting product is dried in a drying drum. The granulate is screened for oversized and undersized particles, which are then recycled into the granulation process. The discharged product is cooled in a cooling drum and/or in a bulk flow cooler. In order to prevent foaming, caking and dust formation, the product is finally coated with some conditioning agents.

3.1.2 Produced TENORM

In frame of the fertiliser production process the raw material phosphate rock as well as the waste phosphogypsum and the products themselves may have to be classified as TENORM. The ^{238}U activity concentrations of the phosphate rocks vary widely in dependence from their geological source, especially sedimentary phosphate rocks show high levels, whereas ^{232}Th is constantly below the TENORM definition limit (table 3-1). In consequence, ^{226}Ra and ^{210}Pb are enhanced in phosphogypsum if ^{238}U was also present in the ores, the concentration factor is of 80%. From fertiliser plants in the central Florida phosphate district (USA) activity concentrations of 1300Bq/kg are reported for both (FIPR, 1998), in Belgium ^{226}Ra concentrations of maximum 3000Bq/kg were even found (POFFIJN, 2002). But in most cases, the phosphogypsum's activity

Table 3-1: Activity concentrations in phosphate ores from different countries (according to ABDULLAH & DAHL, 1995, MARTIN et al., 1997).

country	type of rock	activity concentration [Bq/kg]	
		^{238}U	^{232}Th
China	igneous	150	25
Florida, USA	sedimentary	1500 - 1900	20 - 60
Israel	sedimentary	1500 - 1700	n.d.
Jordan	sedimentary	1300 - 1850	n.d.
Kola peninsula, Russia	igneous	40 - 90	40 - 230
Morocco	sedimentary	1500 - 1700	10 - 200
North Carolina, USA	sedimentary	1100	20
Senegal	sedimentary	2350	n.d.
Tunisia	sedimentary	590	90
western region, USA	sedimentary	8100	n.d.

n.d.: no data available

concentration of ^{226}Ra ranges between 400 and 700Bq/kg as it is mentioned for France, Germany or UK (PENFOLD et al., 1999). Then, in the final fertiliser product up to 90% of the raw material's uranium content can be found, because the phosphoric acid used in frame of the wet process leaches almost all uranium from the initial rock and transfers it into the product (RADULESCU & POPESCU, 2002a). This is the reason for possible enhanced ^{238}U activity concentrations up to 1100Bq/kg in fertilisers, from USA concentrations up to 3000Bq/kg are reported. The progenies ^{226}Ra and ^{210}Pb are usually contained in dimensions of 30-60% (PENFOLD et al., 1999). Special attention must be also paid to discharged waste waters from phosphate ore processing, which can contain elevated radium concentrations. Radium co-precipitates with barium in sulphate-bearing waters as radiobarite [Ba(Ra)SO_4] and POFFIJN & DE CLERK (2004) reported that sediments along river banks being influenced by such waste waters can show maximum ^{226}Ra concentrations of 14,000Bq/kg close to the phosphate plant.

3.1.3 Investigation site

Samples covering the whole production process were provided by a Belgian fertiliser company. Two phosphate rock samples, one from Morocco and due to limited availability one from Kola, one phosphogypsum sample and two fertilisers (NPK- and PK-type) were delivered. The site was not accessible, the company demanded for anonymity.

3.2 Processing of metal ores

There is a wide spread of metals being extracted and then refined and processed worldwide. As a representative of metal processing the Romanian aluminium industry was chosen, for which type of industry bauxite is generally the by far most important raw material. Romania has own exploitable bauxite deposits in the north-western region called "Padurea Craiului", which

geographically belongs to the "Apuseni mountains" and where bauxite is present as lenses in outcropping Jurassic limestone, but additional material must be imported, too, mainly from Brazil and Guinea Bissau. Those imports are processed close to the harbours where the material is unloaded (Tulcea), for the own bauxite deposits processing plants are built in that respective area (Oradea) (RADULESCU & POPESCU, 2002a).

3.2.1 Aluminium industry

Aluminium is the most abundant metal in the earth's crust by 8% and is chemically combined with oxygen, fluorine and silica, but never developed in metallic state due to its non-precious character. That silvery light metal is easy to handle, so a lot of types like thin sheets, wires, rods, chips, powder or foils are usual (FALBE & REGITZ, 1995). It occurs most commonly as the ore bauxite, alumino-silicates are present in clay. Bauxite results from the weathering of parent rocks in humid climate, also called "fossil soil", and may show a significant organic content such as tree roots due to decomposed organic material (MATTHES, 1996). It is rich in aluminium oxides called alumina (55-65%), laterite deposits (enriched in iron) contain up to 35% alumina, therefore the principal aluminium source is bauxite (PENFOLD et al., 1995). Bauxite deposits are relatively shallow (less than 10m) and are mainly exploited by open pit mining. Beside Romania, in Europe commercial deposits of bauxite are located in southern France (there is the location "Les Baux" the name comes from) and Hungary. The main rock forming minerals are boehmite [Al_2O_3 * H_2O] and gibbsite [Al_2O_3 * 3 H_2O], apart from which bauxite is predominantly made up of iron and silica minerals giving a characteristic red colour. Other minor constituents include titanium, potassium, calcium and gallium plus a range of other metallic and non-metallic elements being present in various mineral compounds (ALU, 2006). Aluminium is widely used throughout industry and in larger quantities than any other non-ferrous metal. It is alloyed with many other metals such as bismuth, chromium, copper or silicium in order to give a stronger resistance. The finished products are used in shipbuilding, electrical industry, engineering and building industry, domestic goods production and aircraft and automobile industry as well. A major application of sheets is in beverage and foot containers, fine particulate forms are employed in paints and in the pyrotechnic industry (RP 95, 1999).

The aluminium production comprises two steps: at first alumina is extracted from the bauxite ore based on the so-called "BAYER-process", then the produced Al-oxides are treated by fusion electrolysis in order to obtain pure aluminium. Both processes are shown in figure 3-3 in simplified block flow diagrams.

a) BAYER-process

In 1892, K.J. BAYER developed this processing scheme which extracts alumina from the raw material bauxite (fig 3-3a). In the beginning, the ore is crushed and milled and soda lye (NaOH) is added as disintegration leach. Since gibbsite is more readily soluble in sodium hydroxide solutions than boehmite, it is the preferred mineral (RP 95, 1999). After a period of some hours this mixture is transferred into an autoclave to be heated up to a temperature of 200°C under high pressure conditions. By doing so, the disintegration is performed within 6-8 hours and leads to soda aluminate (CHEM, 2006):

$$Al(OH_3) + NaOH \rightarrow Na[Al(OH)_4] \quad \text{[equ. 3]}$$

In frame of this procedure the iron and silica compounds are kept insoluble. In thickening vessels water is then added at moderate temperatures (90-100°C), which results in the aluminium hydroxide hydrargyllite (CHEM, 2006). The insoluble components are removed during that

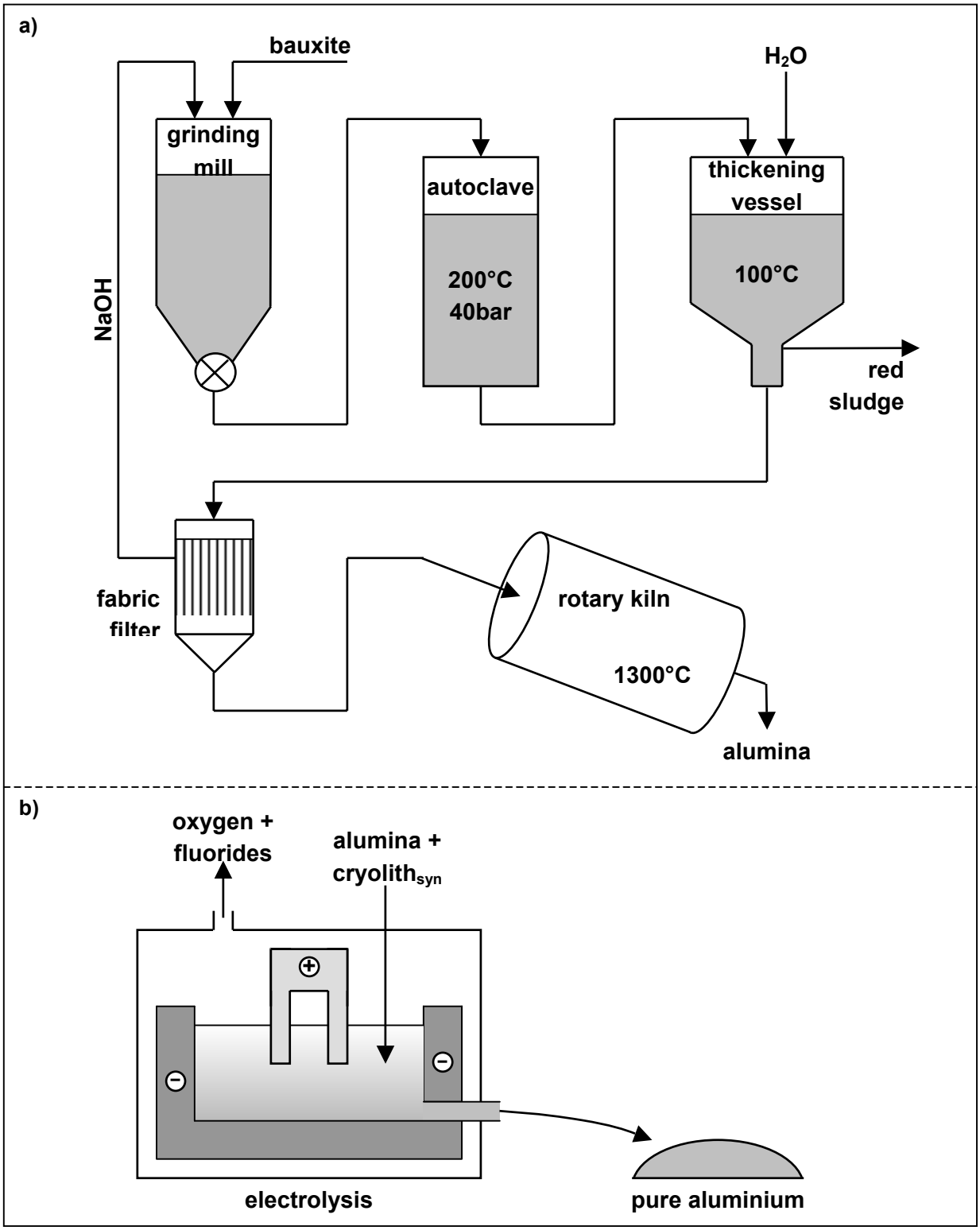

Fig. 3-3: Block flow diagram of aluminium production from bauxite: a) BAYER-process; b) fusion electrolysis (based on GDA, 2002).

process, the created material is called "red sludge" due to its colour caused by the iron and silica oxides. Usually, that residual waste consisting of about 55-60% solid substance is transferred into large tailing ponds close to the processing plant, perhaps later heaped up in stockpiles (RADULESCU & POPESCU, 2002a). After also removing the soda lye by fabric filter to be almost completely recycled, the aluminium hydroxide is calcined in a rotary kiln at temperatures of 1300°C for complete dehydration, so alumina is produced (CHEM, 2006):

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O_4 \qquad \text{[equ. 4]}$$

The waste red sludge is produced in dimensions of 700kg per ton alumina, but it is a potential source of titanium. Other useful by-products from the BAYER-process are 1kg vanadium and 0.1kg gallium per ton alumina (PENFOLD et al., 1999).

b) fusion electrolysis

The obtained alumina are reduced to pure aluminium by fusion electrolysis (fig 3-3b), which was developed independently from each other in 1886 by the French HEROULT and the American HALL as well (CHEM, 2006). First of all, the high melting point of the aluminium oxides (more than 2000°C) must be lowered. For that reason synthetic cryolith [$Na_3(AlF_6)$] is filled into an electrolytic cell and after smelting was reached, alumina is added. The tub made of carbon acts as an electrode, the anodes are carbon sticks being dipped in the liquid and are consumed in frame of the electrolysis by oxidation. Apart from the dissection of the Al-oxides the generated current in the liquid leads to the demanded temperatures ranging around 960°C, so the bath is not to be heated separately (GDA, 2002). The pure aluminium accumulates on the bottom and is periodically evacuated by the means of an aspirator crucible, oxygen and fluorides are volatile by-products. The process is characterised by an immense demand for energy: per ton aluminium 14,000kWh are required at direct current of 4-5V and intensity of 160,000A maximum. In same relation the material consumption amounts 2 tons of alumina being equivalent to 4.5 tons of bauxite, 40kg synthetic cryolith and 500kg anodic carbon (CHEM, 2006).

3.2.2 Produced TENORM

Both the raw material bauxite and the generated waste material red sludge can contain significant radionuclide concentrations. Bauxites may be impured by uranium and thorium due to their geological genesis and depending on that, the resulting red sludge shows then mentionable activity concentrations, too (table 3-2). In frame of the disintegration process by soda lye, uranium, radium and thorium are also leached from the initial bauxite and therefore transferred into the red sludge. According to KRUEGER (1999), interacting silica leads to an almost complete precipitation of uranium during the BAYER-procedure and the uranium concentrations in the separated aluminium hydroxides decrease, if

- the precipitation temperature decreases
- the surface of the crystals increases
- the concentration of organic carbon in the solution decreases

Table 3-2: Activity concentrations in bauxites and red sludge (according to KRUEGER, 1999, JUHASZ & SZERBIN, 2002, RADULESCU & POPESCU, 2002a).

material	activity concentration [Bq/kg]		
	^{238}U	^{226}Ra	^{232}Th
bauxite from Pijiguaos (Brazil)	90	n.d.	665
bauxite from Trombeta (Brazil)	500	1500	85
bauxite from Boke (Guinea Bissau)	210	270	110
bauxite from Csordakút (Hungary)	850	800	450
red sludge from Csordakút (Hungary)	950	570	400
red sludge from Oradea (Romania)	1580	1675	45
red sludge from Tulcea (Romania)	185	210	250

n.d.: no data available

Usually, red sludge is not used further on and remains in the tailing ponds or stockpiles respectively and due to its high moisture content, dust emissions are not to be expected (KRUEGER, 1999). But in some very rare cases that muddy material is used for baking bricks, which then also have some elevated activity concentrations, PENFOLD et al. (1999) mentioned 250Bq/kg of ^{226}Ra and 370Bq/kg of ^{232}Th. The final product aluminium is generally not contaminated by natural radionuclides apart from the only exemption reported by PENFOLD et al. (1999) to show ^{238}U concentrations of 360Bq/kg.

3.2.3 Investigation site

The investigation site is located in the far East of Romania aside from the city Tulcea, close to Ukraine. The company was formerly known as "Alum Tulcea", in 1996 it became privatised and was taken over then in 2006 by "Alro-Slatina", an aluminium producer and the main client (CTUL, 2006). The bauxite processing started in 1973 and it is still the biggest alumina plant in Romania with an alumina production of 600,000 tons produced by 1500 people in 2004 (WAGNER, 2004). As a result of that huge capacity, the generated red sludge is also immense: 420,000 tons in 2004 (GOR, 2004). That waste material is transported as suspension by pipeline to a tailing pond, which is located 10km to the Southwest of the city and occupies 3km^2 roughly (fig. 3-4) (RADULESCU & POPESCU, 2002a). The bauxite ore is exclusively imported from Brazil and Guinea Bissau being reported to contain radionuclides of the ^{238}U decay series (table 3-2). The resulting red sludge may therefore be contaminated, too. Gamma dose rate measurements on the sludge's surface within the pond were undertaken by RADULESCU & POPESCU (2002b) and resulted in values around 300nSv/h.

The samples for investigations were provided by the "National Research & Development Institute for Metals and radioactive Resources" (ICPMRR), Bucharest, and comprise imported bauxites from the Brazilian Trombeta-zone and the Boke-zone in Guinea Bissau as well. Red sludge was delivered from the Tulcea tailing pond. Direct access to the site was not enabled.

Fig. 3-4: Location of the Tulcea bauxite processing plant and the red sludge tailing pond (small Romania-map from www.fifoost.org/rumaenien/rumaen-karte.gif; Tulcea-map from RADULESCU & POPESCU, 2002a).

3.3 Mineral sand processing

In fact, the mineral sand processing industry is mainly based on two minerals: zircon and monazite respectively chemically similar ones.

Zircon [$ZrSiO_4$] contains zirconium which is an irreplaceable raw material for the manufacture of refractory components and abrasives as well. It is also used in fine ceramic production acting as an opacifier in glazes and enamels and as an additive in special glass. Zirconium metal is widely used in the nuclear power generation due to its low absorption cross-section for neutrons and high resistance to corrosion inside atomic reactors whilst zircon bricks are used as linings for glass furnaces (MARTIN et al., 1997, PENFOLD et al., 1999). Another important zirconium bearing mineral beside zircon is baddeleyite [ZrO_2]. Besides as accessories in magmatic rocks both are found accumulated in sands along river banks or beaches due to their characteristic high density [zircon: 4.7g/cm^3, baddeleyite: 5.5g/cm^3; GRAUBNER, 1980]. Commercially relevant deposits of zircon are located in Australia, India, Ukraine, Malaysia and USA, baddeleyite is exploited in Brazil, Sweden, India and Italy (PENFOLD et al., 1999). The

sands are typically pre-processed in very large quantities by gravimetric and electromagnetic sorting to separate the mineral sands. During this process a lot of dust is generated, because the initial grain size of 100 to 200µm is reduced to 2µm, in some cases also by additional milling (RP 95, 1999).

Monazite [(Ce, La, Nd, Th)PO_4] is demanded due to its high content of rare earth elements [REE], also bastnaesite [(Ce, La, Nd, Th)(CO_3)F] is an important source of REE. Commercially useful deposits of both monazite and bastnaesite are found in Brazil, India, USA and Australia. They are also occurring as accumulated mineral sands and the sorting is done in the same way as described for zircon and baddeleyite (PENFOLD et al., 1999). REE comprise the group of lanthanides, which are used as components in Mg-alloys and in frame of high-tech production as permanent magnets or supra-conductors. Furthermore, they are also applied for glass colouring, enamel and ceramic production and burnishing. In Europe, there are two important producers dealing with REE: the "Treibacher Industrie AG" in Austria and "Rhodia Terres Rares" (formerly known as „Rhone Poulenc"), France (GELLERMANN et al., 2003).

As a representative of mineral sand processing the refractory industry was chosen.

3.3.1 Refractory industry

The refractory industry manufactures heat-resistant materials that constitute the linings for high-temperature furnaces and reactors and demands therefore for physically persistent and chemically consistent components. For that purpose mullite [3 Al_2O_3 * 2 SiO_2] is the material of choice, because due to its geological origin under extremely high temperatures, it also withstands high temperatures and strength and is shock resistant (KMC, 2005). Since the only naturally occurring mullite deposit worldwide is known from the Isle of Mull, UK (that is the locality the name comes from), it must be produced synthetically from the group of aluminosilicates [Al_2SiO_5] (KMC, 2005). Those latter comprise the polymorph mineral variants andalusite (made under moderate temperature and low pressure conditions), sillimanite (high temperature, moderate pressure) and kyanite (high temperature and pressure) (MATTHES, 1996). According to USGS (2006), the starting material is a mixture of either alumina and silica or bauxite and kaolin, which is heated up to temperatures higher than 2000°C in electric arc furnaces (fig 3-5). By doing so, the materials are calcined and transformed into a liquid state, under which conditions the chemical combination Al_2SiO_5 is no longer existent to be converted into unbound Al_2O_3 and free silica (MATTHES, 1996):

$$3\ Al_2SiO_5 \rightarrow 3\ Al_2O_3 * 2\ SiO_2 + SiO_2 \qquad \text{[equ. 5]}$$

The further processing is described according to TREIBZ (2006), by which company the samples were delivered. In this study fused zirconia mullite [FZM] is investigated, therefore zircon sand is also filled into the furnace. In frame of the fusion process a lot of dust is emitted to be collected by filters. The resulting FZM is cooled down for more than a week in a cooler. The next step is to crush and mill the mullite, so the obtained granulation is then sieved and grain sorted in sedimentation tanks, because the grain size is an important characteristic for the use of the

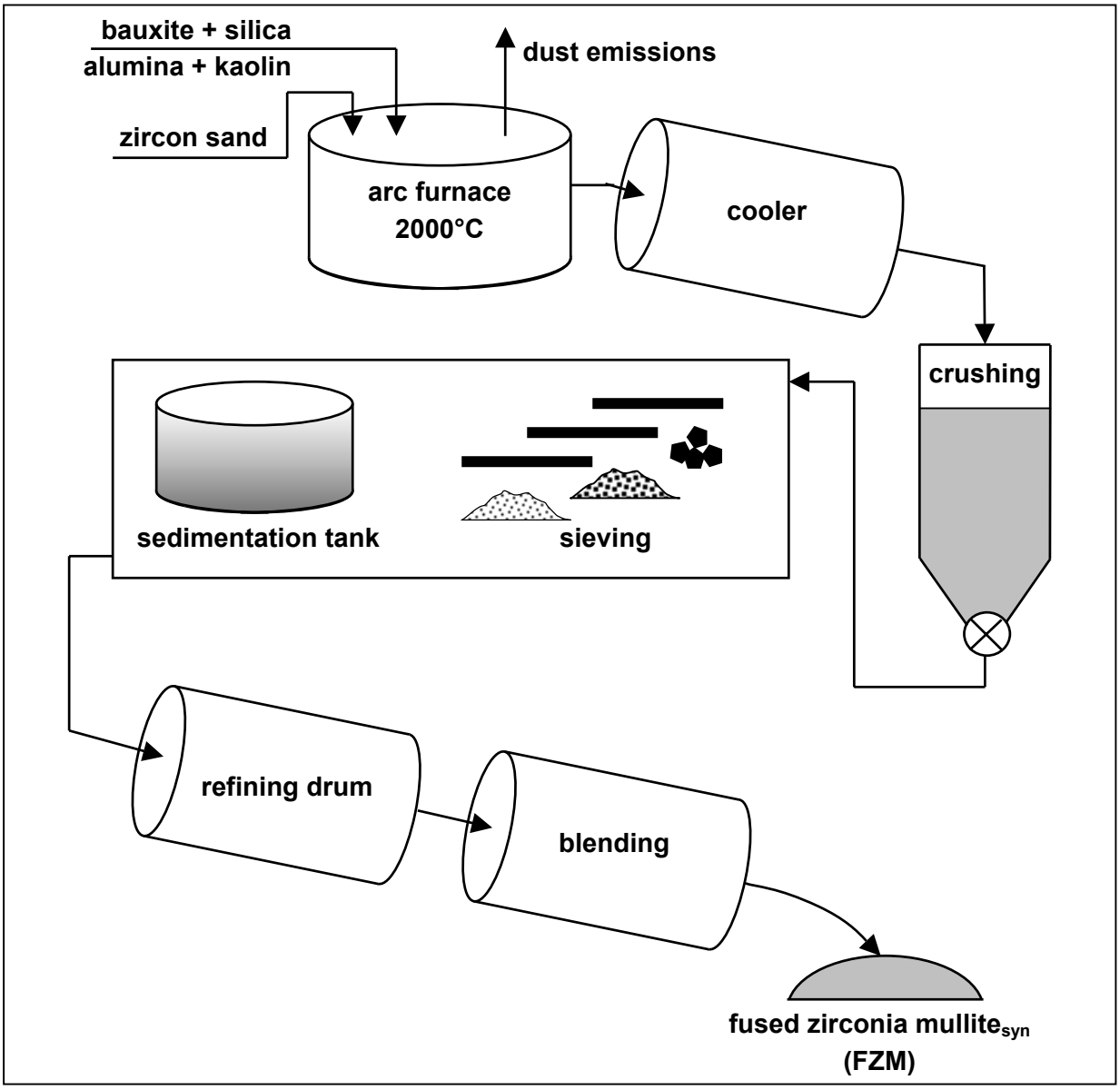

Fig. 3-5: Block flow diagram of the production process of synthetic fused zirconia mullite [FZM] from a mixture of bauxite and silica or alumina and kaolin to be refined by zirconium (based on TREIBZ, 2006, USGS, 2006).

material later on. The refining processes depend on the special properties the products shall have, the last steps are blending and a finally sieving. As mentioned by USGS (2006), 1.15 tons of mineral concentrate are needed to obtain 1 ton of mullite.

3.3.2 Produced TENORM

The raw material mineral sands of both zircon and monazite contain accessorily uranium and thorium, so these radionuclides and progenies are also brought in the respective manufacturing processes. Pegmatites are reported to contain both radionuclides in dimensions of some ten thousands Bq/kg, those and other activity concentrations for mineral sands are listed in table 3-3 according to PENFOLD et al. (1999). It is obvious that the mineral containing sands show much lower concentrations than the pure minerals themselves due to impurities and other ingredients. Nevertheless, dose rate calculations for 1m distance from zircon sand storage tanks

Table 3-3: Activity concentrations in zircon and monazite substances (PENFOLD et al., 1999).

raw material	activity concentration [Bq/kg]		
	^{238}U	^{226}Ra	^{232}Th
zircon in pegmatites	12,000 - 74,000	n.d.	16,000 - 40,000
zirconium oxides	5500	n.d.	440
zircon sand	n.d.	3700	600
monazite sand	375	n.d.	1800
monazite	up to 40,000	n.d.	up to 3,000,000

n.d.: no data available

as well as on top of the tanks resulted in values of 5mSv/a under worst circumstances (UNSCEAR, 1988). The first treatment step for the sands is the gravimetric and electromagnetic sorting, which is a potential dusty process and therefore radionuclide bearing dust may be generated and distributed indoors (RP 95, 1999). Taking 10,000Bq/kg of ^{238}U as the basis for zircon sand (table 3-3), the resulting dose in the vicinity is of 4-6mSv/a (SCHOLTEN et al., 1993). In case of producing fused aluminium oxides such as FZM also the raw material bauxite can contain enhanced levels of radionuclide concentrations depending on its source (table 3-2). The heating of the raw material's mixture up to temperatures of 2,000°C and more may lead to volatilised ^{210}Pb and ^{210}Po, which are then accumulated in the filters. As reported by PENFOLD et al. (1999), fume from arc furnaces used for refractory production in UK contained activity concentrations of both ^{210}Pb and ^{210}Po up to 500,000Bq/kg.

3.3.3 Investigation site

The company having provided the sample material is the "Treibacher Schleifmittel Zschornewitz GmbH", one of two German agencies of the Austrian company "Treibacher Industrie AG" located in Treibach, Carinthia, the other German one is located in Laufenburg (TREIB, 2006). That parent company was founded in 1898 by Carl Auer von Welsbach as "Treibacher Chemische Werke" and deals with chemical compounds in order to produce abrasives (bound and coated), refractory materials, ceramics and blasting media (TREIBZ, 2006). The total number of employees ranged around 600 in the last 5 years, the sales were of about 600Mil € in 2005 (TREIB, 2006). The delivered samples comprise the raw material zircon sand, the waste material filter dust collected during the fusion process and the final product FZM of different grain sizes (1.5-3.0mm and milled). Direct access to the company was not possible.

3.4 Crude oil and natural gas extraction

Crude oil is of an immense importance for a widespread of products and applications. It is the starting material for fuel production, which is undertaken in refineries by atmospheric distillation leading to different weighted fractions such as heavy oil for ship engines and heating units, medium distillates like kerosene for airplanes or light oils like petrol for cars. The residue

from that process is further distilled under vacuum conditions to produce different lubricants. Crude oil is also the basis for many products made by the chemical industry and the residue from the vacuum distillation (bitumen) is used for road construction. Natural gas is widely used for energy production and is also inevitable for some products of the chemical industry (EISNER et al., 1986).

Crude oil and natural gas are hydrocarbons and need special geological conditions to be formed. They are generated from died off marine animals and plants, especially plankton, which sank to the sea-bottom and were accumulated in the sediments. If those sediments were then exposed to certain temperatures and pressures ranging around 135-150°C and 300-800bar (equivalent to a depth of 1-3.5km), also named "oil window", for a sufficiently long period, crude oil was created. The generation temperatures and pressures for natural gas range around 120-200°C and more than 500bar ("gas window"). Therefore, the sediments had to remain long enough under those conditions, which means the sediment basin had not sunk rapidly (BAHLBURG & BREITKREUZ, 1998). In many deposits both crude oil and natural gas occur simultaneously, but isolated gas deposits are also known due to possible exhalations from other hydrocarbons such as coal. Once formed, oil and gas must have been accumulated in special rock formations (e.g. a porous anticline being covered by an impermeable rock layer) in order to create an exploitable deposit. According to DE LUCA (1999), today a third of the exploited crude oil deposits are located offshore, for natural gas it is given by a quarter. It is expected that this will be changed basically in the future, because more than 90% of the world's undiscovered reserves are estimated to lie offshore, beyond the continental shelves (fig 3-6). That also involves that the water depths for exploratory drilling and extraction are expanding. In the 1960s the limit was of about 300m, by the early 1990s explorations were undertaken in depths of 2000m and more. So the term "deepwater" commonly used in oil geology has now changed into "ultra-deepwater" and there are innovations in progress for production facilities to rise 3000m in the nearest future (SKAUG, 1998).

3.4.1 Extraction processes

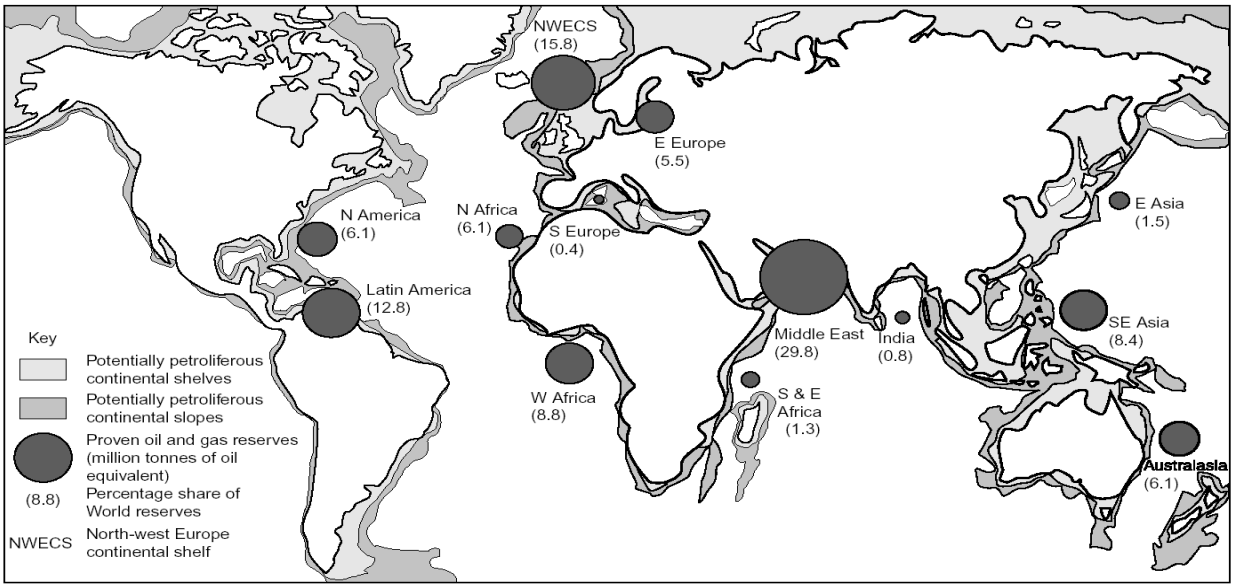

Fig. 3-6: Potentially petroliferous offshore zones and regional distribution of proven offshore crude oil and natural gas reserves (DE LUCA, 1999).

In 1858, one of the very first oil wells worldwide was drilled successfully in Wietze, a German village in Lower-Saxony. In those times a deposit was to be exploited to a maximum of 10-20% of the initial oil volume (DEW, 2006). Today, exploitation rates of 50% are possible due to special procedures such as the so-called "secondary procedure" (flooding by water) or "third procedure" (pumping steam into the well, perhaps also mixed with tensides). In general, there are two basic types of extracting a crude oil or natural gas deposit (PINDER, 2001):

1. **Eruptive extraction**
   The reservoir rock is characterised by high pressure, so the oil or gas is naturally forced to ascend in the well.
2. **Pumping extraction**
   The pressure in the reservoir rock is too low or absent, so pumping facilities must be installed in the oil bearing formation.

Wells are designed in a telescope-style and taper by depth. Today, wells can also be drilled horizontally enabling a deposit exploitation by just one or a few platforms (e.g. the German offshore oil field "Mittelplate" being tapped from one onshore platform) (NLFB, 2002).

Whereas onshore oil drilling units are usually constructed fix, the offshore production platforms can vary as fixed or mobile installations depending on the size of the exploited deposit respectively the field output, sea conditions, the water depth or the expected term of production (fig. 3-7). As carried out by PINDER (2001), the mobile "jack-up"-rigs were used firstly and comprised a working platform having been equipped with a drilling rig, which was floated during transportation. In the operational location it was then raised out of the water and the platform's

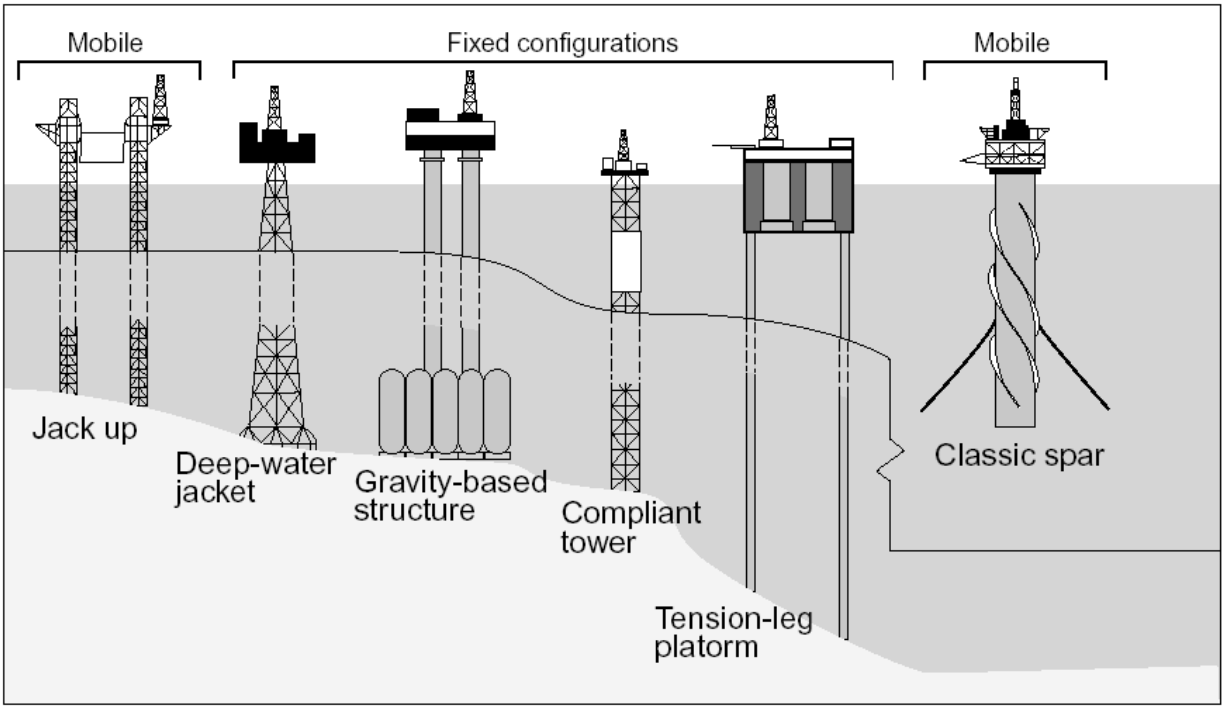

Fig. 3-7: Different offshore platform constructions in fixed as well as mobile variations (PINDER, 2001).

legs were lowered down to the seabed. The "deepwater jacket" is a tall pyramidal pylon fixed to the seabed and equipped with an operational platform at its apex, its strength is derived partly from the pylon's width and pyramidal shape, but also from its geodetic steel construction. "Gravity-based structures" involve preparations on the seabed of a level foundation on which the rig can rest. The working platform is supported by tubular columns fixed at the base to ballasted chambers, holding the entire structure in place through the force of gravity. A third fix configuration is the "compliant tower". As with the deepwater jacket, this is fixed to the seabed, has a geodetic steel construction and is surmounted by the working platform. Its particular feature is that the tower itself includes a midsection incorporating providing a degree of flexibility in the structure and therefore resistance to stress. All these fixed-rig types of structure reach their limits towards outlying slopes of the continental shelves. But the "tension-leg platform" can also be applied in deeper waters due to its relatively lightweight, tubular fixed legs. A floating superstructure carries all operational facilities, which supports its own weight and stabilises by upward tension. In contrast, the "classic spar" is a mobile hollow column of circular cross-section, which sits vertically in the water and is supported by buoyancy chambers at the top. Positioning is not achieved by fixed legs, but by anchored cables in tension. Additional stability is provided by the length of the column itself, which effectively acts as the keel of the "vessel", and by a mid-structure suspended from the buoyancy equipment. The working platform surmounts the floating column allowing operations to be conducted through the protected environment of the hollow core. Nowadays, the so-called "floating production, storage and offloading" (FPSO) facilities are an interesting alternative. This concept is based on a converted supertanker, which moors above the wellhead and has capacities to store extracted oil ready for transshipment to visiting tankers. In one sense it is a fixed facility, because the ship remains at the same location for an extended period, but as a purpose-built tanker it retained its full ocean-going certification and if necessary, it can be redeployed even more rapidly than spars to new production sites (PINDER, 2001).

3.4.2 Produced TENORM

The type of rock the oil or gas bearing formation is made of largely determines the natural radionuclide concentrations in that reservoir. Most important reservoir rocks are carbonates, limestones and shales beside coal in some extent. From these rock types black shales being characterised by a high content of organic carbon do have the highest activity concentrations, mainly of uranium and then progenies, which can be assumed to be in secular equilibrium. This is due to the fact that the reducing milieu caused by organic components acts as a geochemical sink when uranium bearing waters ascend and get in contact with the carbon (VON PHILIPSBORN, 1998). It has been found that dense black organic matter, sometimes called asphaltite, contains as much as 1% uranium by weight, however crude oil itself is rather low in uranium content (up to 2Bq/kg U_{nat}) (PIERCE et al., 1955).

In frame of almost all operations during hydrocarbon production huge amounts of liquid, solid and gaseous wastes are generated and all can be affected by enhanced concentrations of natural radionuclides. The by far most important solid materials from the radiological point of view are scales and sludge respectively undifferentiated precipitations (table 3-4). According to

Table 3-4: Activity concentrations in substances from oil and gas extraction (KOLB & WOJCIK, 1985, PENFOLD et al., 1999).

material	activity concentration [Bq/kg]				
	^{238}U	^{226}Ra	^{210}Pb	^{228}Ra	^{228}Th
scales	undifferentiated total activity: 5000 - 500,000				
$scale_{oil}$	n.d.	max. 300,000	n.d.	max. 390,000	max. 48,000
$scale_{gas}$	n.d.	max. 1,000,000	max. 70,000	max. 360,000	max. 26,000
scale from offshore oil platform	500	250,000	12,000	25,000	300,000
sludge	undifferentiated total activity: 500 - 50,000				
sludge from offshore oil platform	n.d.	25,000	n.d.	2600	30,000
precipitation in installations	n.d.	max. 1,000,000	max. 72,000	max. 360,000	max. 200,000
precipitation in oil well	< 900	1,100,000	n.d.	n.d.	n.d.
sand	n.d.	8900	60	2300	10,000

n.d.: no data available

WOODALL (2001), petroleum formation waters, which are derived from the oil or gas reservoir as an accompaniment in frame of extraction, have generally high saline concentrations (more than seawater) and carry barium, calcium, strontium and radium (all are alkaline earth metals). In addition, seawater is frequently injected into the well for enhancing the production by maintaining the pressure (GODOY & PETINATTI DA CRUZ, 2003), sometimes the raised brines are re-injected, too (KOLB & WOJCIK, 1985). During the extraction process, barium dissolved in the brines precipitates inside the tubes' walls and other installations as scale, which is caused by pressure and temperature changes, and radium-isotopes are then co-precipitated due to similar chemical characteristics, the resulting material is called radiobarite [$Ba(Ra)SO_4$] (WEISS, 2003). Contaminated sludge results from the drilling process itself or is left behind in the sumps of separation vessels, but its radionuclide concentrations are generally lower (table 3-4).

Since radium is very soluble in saltwater but not in oil, the prime source of radiation in the generated solid wastes is caused by ^{226}Ra and ^{228}Ra whereas the product is to be considered as radium free (GODOY & PETINATTI DA CRUZ, 2003). The long-living daughter products ^{210}Pb and ^{228}Th regrow in relation to their physical half-lives, which means the specific activity of ^{210}Pb will grow up to that of ^{226}Ra in a volatile dense zone, that of ^{228}Th will exceed the ^{228}Ra activity by a factor of 1.4 (transitory equilibrium). Sometimes ^{210}Pb is enriched against ^{226}Ra if the connate waters contain high amounts of lead (WEISS, 2003).

Unlike radium, radon is highly soluble in petroliferous substances and less soluble in water (WHITE & ROOD, 2001). Therefore, radon is especially exhaling from oily sludge and when the latter is settled, ^{210}Pb accumulations occur, beside elevated radon concentrations, in volatile dense zones such as tubes, pipelines, vessels or storage tanks. But nevertheless, dissolved radon may also be found in brines and produced waters. In frame of natural gas extraction, special attention

must be paid when the gas is liquefied for storage or transportation, because radon is associated with natural gas on an average of 1kBq/m^3 (UNSCEAR, 1988) and its boiling point is of -61.8°C ranging between those of the hydrocarbons ethane (-88.6°C) and propane (-42.1°C). Consequently, radon tends to follow the propane stream in separators and much of the radon is removed as well during that process (GRAY, 1990 & 1993).

Since the generated scales and sludge contain also mentionable amounts of mercury, a demanded raw material, and a special procedure was developed in the last decades for separating that element (GMR, 2007). After the selective purification the sludge or the scales still contain the same specific activity as before, the recycled mercury is of highest purity. The residues - in case of sludge after partial dewatering - are then mixed with Geopolymer® [a high-alkali (K-Ca)-Poly(sialate-siloxo) binder (DAVIDOVITS, 1988)] for immobilisation (LARUE et al., 2002). In frame of that procedure also the occurring radionuclides are fixed by the binder and can be considered as being immobile. The sludge or the scales, that means waste, are going to be again a waste after demercurisation, but they can be stored for example at dump-sites according to legal frame conditions. In earlier times, it was usual to backfill the initial waste of scales and sludge into the bore holes. Today, that proceeding is only allowed by the responsible Mining Authority if a migration of mercury into the groundwater can be excluded (WEISS, 2003).

3.4.3 Investigation site

The investigated samples represent both the most important and voluminous solid waste materials, which occur in frame of oil extraction: sludge and scales were delivered twice in each case. They resulted from onshore oil extraction in Germany, but the providing company demanded for anonymity.

3.5 Hard coal extraction

In general, coal is almost exclusively used for energy production by combustion, in some cases after refining to coke such as iron and steel production. It has been formed under warm and moist conditions from peat, which is the most common settlement in swamps such as delta-areas of large rivers. Those sediments consisted initially of huge amounts of plant remnants, which were then altered during time due to physical and chemical processes and absence of oxygen. The altering was caused by increasing temperatures and pressures when the sediments have been sunk into deeper regions. This diagenetic process was connected with a relative enrichment of carbon and lead to coal seams finally. Temperature and pressure are the determining parameters for the created type of coal: brown coal is formed up to a depth of 1.5km being equal to 80°C and 400bar, if both are arising hard coal is formed and beyond 200°C and 800bar anthracite is the result (BAHLBURG & BREITKREUZ, 1998). Pure carbon is formed by metamorphosis and is called graphite. According to the carbon content, different classes of coal are introduced (table 3-5). The higher the carbon content in the coal the higher is the heating

Table 3-5: Coal classification by carbon content and heating coefficient (according to BAHLBURG & BREITKREUZ, 1998, MÜLLER, 1977).

material	depth [km]	classification	carbon content [%]	heating coefficient [MJ/kg]
wood	0	wood	50	19
peat	< 0.1	peat	55 - 59	21 - 23.9
brown coal	0.1 - 1.5	lignite	60 - 70	24 - 28.1
		sub-bituminous coal	70 - 78	28.2 - 31.1
hard coal	1.5 - 3.5	bituminous coal	79 - 84	31.2 - 34
		semi-bituminous coal	85 - 90	34.1 - 36.5
anthracite	> 3.5	anthracite	91 - 98	36.6 - 34.4
graphite	metamorphosis	graphite	99 - 100	34.3

coefficient (MÜLLER, 1977) and therefore, hard coal is the preferred type of coal for energy production due to its efficiency (anthracite is rarely exploitable).

3.5.1 Extraction and processing procedures

Usually, brown coal is mined in open pits by large excavators. This is due to the lower depth where it is formed, e.g. in Germany the maximum depth is of 300m below the surface. Therefore, huge amounts of non-coal-bearing material must be removed, too, and are heaped up close by to be used again for land reclamation later on. Hard coal is mostly mined in underground pits by cutting the coal seam, which was formed in deeper layers. The coal is transported by conveyors through galleries and by elevators in shafts to the surface. In 2006, German hard coal is extracted from maximum depths of 1500m below the surface (Northern Ruhr district) (STP, 2006). Also this mining style is characterised by some amounts of dead rock, which are brought to the surface and heaped up in stockpiles, but by far not so many as in frame of open pit mining. One contrary example for hard coal extraction by open pit mining is Kentucky, USA, where the coal seams were geologically pushed back closer to the surface (KGS, 2006a). In frame of underground mining, especially the galleries must be kept continuously ventilated to prohibit accumulations of methane, which is exhaled from the organic coal seams and can cause disastrous explosions. Also formation waters must be pumped to the surface, which are then discharged into sewers or rivers as pit water.

The mined coal is transported to power plants by trains, barges or trucks (KGS, 2006b). A block flow diagram of such a coal fired power plant is shown in fig. 3-8. The first processing step is to grind the coal to powder. That powdered coal is then blown by a blast into the combustion chamber of a power boiler to be burnt up to 1400°C. The boiler is surrounded by pipes filled with water, which is then vaporised. That superheated high-pressure steam passes through a turbine being connected with a generator and forces the turbine propellers to rotate at high

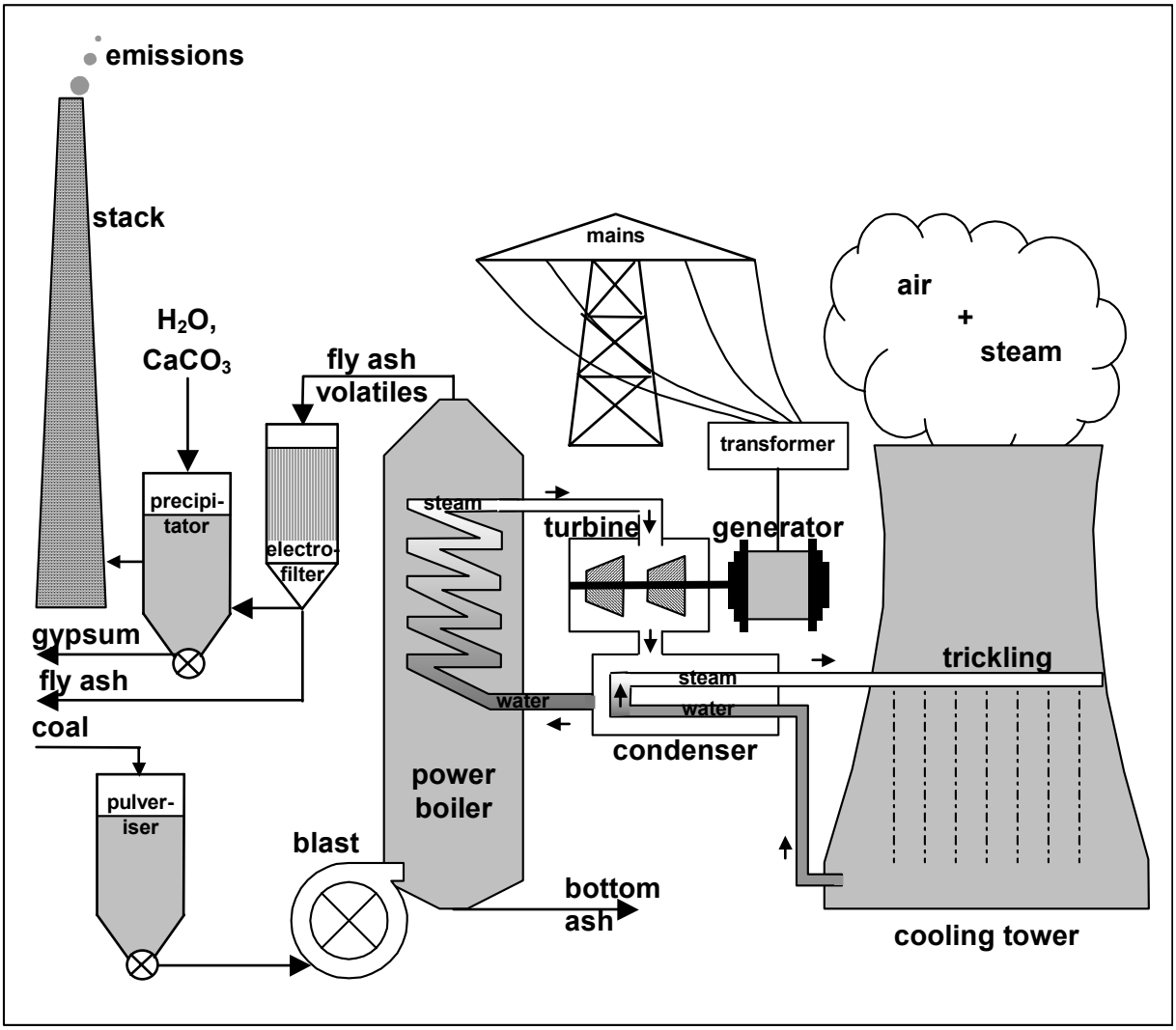

Fig. 3-8: Coal fired power plant (based on BUE, 2006).

speeds creating electricity in the generator. After the steam has passed the turbine and delivered its energy, it is cooled down in a condenser to become again a part of the heating cycle. In the condenser a second water-steam-cycle provides the cooling and the steam generated there is cooled in large cooling towers by trickling and air. The produced electricity is transformed into high voltage and then introduced into the mains (STEAG, 1988, BAUMBACH, 2005).

In frame of the combustion process several waste materials are created in both solid and gaseous condition. The coal burning results in two types of ash: on the one hand glassy particles of the melted coal ash settles at the base of the combustion chamber and is periodically removed as bottom ash, on the other fly ash travels upward inside the power boiler with other volatiles (KGS, 2006b). Fly ash consists of solid non-combustible substances such as dust and soot, which are captured by an electro-filter due to electrostatic interactions and are then disposed. According to MARTIN et al. (1997), both types of ash, whose production proportion is of 25% bottom ash and 75% fly ash, are either disposed in landfills or at sea or they are also used as additives for road construction, as substitutes for cement or filling material for concrete. Volatiles include carbon dioxide [CO_2], sulphur oxides [SO_x] and nitrogen oxides [NO_x], of which the sulphuric compounds are removed by a precipitator. That process called "desulphurisation" is based on the

reaction of sulphur dioxide with carbonate [$CaCO_3$] and water resulting in gypsum [$CaSO_4 * 2 H_2O$] and carbon dioxide (EISNER et al., 1986):

$$CaCO_3 + 2 H_2O + SO_2 \rightarrow CaSO_4 * 2 H_2O + CO_2 \quad \text{[equ. 6]}$$

The produced gypsum, also called "energo-gypsum" (LACIOK et al., 2002), falls out of the gas to the bottom of the precipitator and is then removed. Roughly estimated, energo-gypsum is generated in dimensions of 200,000 tons per GW-year and is widely used for the production of plaster and other construction materials (SCHOLTEN, 1995). Beside dust, the remaining stack emissions mainly consist of carbon dioxide, which can be influenced by the mixture of different coals, and nitrogen oxides being controlled by the combustion chamber's temperature (KGS, 2006b).

3.5.2 Produced TENORM

As obvious from table 3-6, the different types of coal usually do not contain strongly enhanced radionuclide concentrations. One exemption is reported by WINGENDER (1995) for hard coal having been extracted in Freital, East Germany. Due to the fact that the coal there is interspersed by uranium, high ^{238}U concentrations up to 15,000Bq/kg were measured. In the former German Democratic Republic (GDR), those coals have been used for combustion until the 1960's, later on only the uranium content was exploited (HENNINGSEN & KATZUNG, 1998). In frame of general hard coal extraction, special attention must be paid to pit waters, which are pumped to the surface as high mineralised brines and discharged into sewers or rivers, because they can contain elevated activity concentrations, especially of radium, due to ion exchange processes in the aquifers (WIEGAND & FEIGE, 2002). If the surface waters bear sulphate, the radium co-precipitates with that barium of the brines resulting in radiobarite [$Ba(Ra)SO_4$], which settles along the sewers' and rivers' banks and is also accumulated in sewage sludge formed in purification plants. Beside the German hard coal mining area Ruhr district, this phenomenon is well investigated in the Polish region of Upper Silesia by CHALUPNIK et al. (2001), too. In dependence from the discharge point, the banks' sediments can show enhanced ^{226}Ra concentrations up to 15,000Bq/kg (SCHMIDT & WIEGAND, 2003), in Poland 50,000Bq/kg are reported, whereas the ^{228}Ra concentrations are lower in both countries (table 3-6). In frame of the coal combustion in power plants, the resulting fly ash can be especially contaminated by ^{210}Pb and ^{210}Po as well, the latter might be almost twice of the lead activity concentration (MARTIN et al., 1997). Nevertheless, also ^{238}U, ^{226}Ra and ^{232}Th can be present in elevated dimensions, BECKER et al. (1992) reported maximum enhancement factors of 17 for the uranium and 15 for the thorium decay series compared with the activity concentrations initially contained in the coal. The combustion of that special coal mined in Freital as mentioned above is reported to result in slag containing ^{226}Ra concentrations up to 4000Bq/kg (RÖNSCH, 1996). The energo-gypsum produced by the desulphurisation process is usually not affected by enhanced radionuclide concentrations (BECKER et al., 1992). But contrary, fractions of the initial activity concentrations can be released by stack emissions and therefore be distributed in the power plants' vicinity. It is written the factors are of 3% for older plants and of 0.5% for newer ones (UNSCEAR, 1988). The specific radionuclides being most noticeably expelled via the stack are ^{222}Rn, ^{210}Pb and ^{210}Po, because they

Table 3-6: Activity concentrations in substances from coal extraction and combustion ([1]BMU, 2000, [2]CHALUPNIK et al., 2001, [3]JUHASZ & SZERBIN, 2002, [4]LACIOK et al., 2002, [5]MARTIN et al., 1997, [6]MICHALIK, 2002, [7]SCHMIDT & WIEGAND, 2003).

material	activity concentration [Bq/kg]			
	^{238}U	^{226}Ra	^{210}Pb	^{232}Th
German brown coal[1]	n.d.	max. 50	n.d.	max. 60
German hard coal[1]	n.d.	max. 150	n.d.	max. 70
Czech hard coal[4]	max. 230	n.d.	n.d.	n.d.
Hungarian hard coal[3]	max. 430	n.d.	n.d.	max. 110
German coke[1]	n.d.	max. 30	n.d.	< 20
German bitumen[1]	n.d.	< 20	n.d.	< 20
German pit waters[7]	n.d.	max. 15 [Bq/l]	n.d.	n.d.
Polish pit waters[2]	n.d.	max. 25 [Bq/l]	n.d.	n.d.
German sediments influenced by pit water[7]	n.d.	max. 15,000	n.d.	max. 6500
Polish sediments influenced by pit water[2]	n.d.	max. 50,000	n.d.	max. 6400
fly ash[5]	200	n.d.	2400	n.d.
Polish fly ash[6]	n.d.	400	n.d.	200
Czech ash[4]	550	140	n.d.	370
Hungarian ash[3]	310	290	400	220
gypsum[5]	n.d.	170	n.d.	20
stack releases[5]	typical annual activity releases per GW-year [Bq]			
	^{238}U	^{226}Ra	^{210}Pb	^{232}Th
	$5 * 10^8$	$5 * 10^{10}$	$1 * 10^9$	$5 * 10^8$

n.d.: no data available

are more volatile and vaporise between room temperature (radon) and a few hundred degrees Celsius (lead and polonium) (MARTIN et al., 1997). In vaporised state it is not possible to filter them out completely by regular ash recovery systems. On the particles which escape filtration, there is a tendency for the volatile radionuclides to associate with smaller ones, thus leading to an increased activity concentration with decreased grain size. These aerosols are of highly radiological relevance, because they are within the respirable range below 10µm diameter, which allows them to penetrate into the pulmonary system (ROECK et al., 1987). The influence of such a radionuclide pollution is estimated in UNSCEAR (1988), where an additional effective dose of 20µSv/a caused by older power plants and 1µSv/a by newer ones are reported to be due to inhalation of long-living natural radionuclides. External radiation and ingestion of contaminated plants cultivated in the power plants' vicinity are responsible for a further additional dose in the same dimension after 20-30 years of the power plant's operating time.

3.5.3 Investigation site

Since river sediments affected by pit waters can show the highest concentrations of natural radionuclides in solids from hard coal mining, such sediments were taken in the North-western Ruhr-district, close to the city of Rheinberg. This region is investigated in detail by FEIGE (1997), SCHMIDT (2001) and SCHMIDT & WIEGAND (2003) as well. The underground hard coal mining pits are located to the left from the north-westwards flowing river Rhein and discharge their pit waters into the small tributaries called "Moersbach" and "Fossa Eugeniana", an artificial sewer constructed in 1621 by order of Infanta Isabella Clara Eugeniana, a daughter of the Spanish King Philippe II. (KINDER & HILGEMANN, 2001). According to LINEG (1995), the amount of pit water annually discharged into the Fossa Eugeniana is estimated at 7.8 * $10^6 m^3/a$. In Rheinberg, both tributaries are combined and then called "Rheinberger Altrhein", northwards from Rheinberg the name is changed into "Alter Rhein" and there the sediment samples were collected along the river banks (fig. 3-9). The samples U-S-1 and U-S-4 were taken from the left river side of the northwards flowing "Alter Rhein", the samples U-S-2 and U-S-3 were taken at the right side. U-S-1 is taken from an unaffected area as background sample whereas U-S-2 represents a flood plain soil being irregularly affected by flood events. U-S-3 and U-S-4 are taken at the riverside close to the waterline, the first one from slip-off slope, the latter at undercut slope. The sample name classification is given in chapter "4. Material preparation and examination methods".

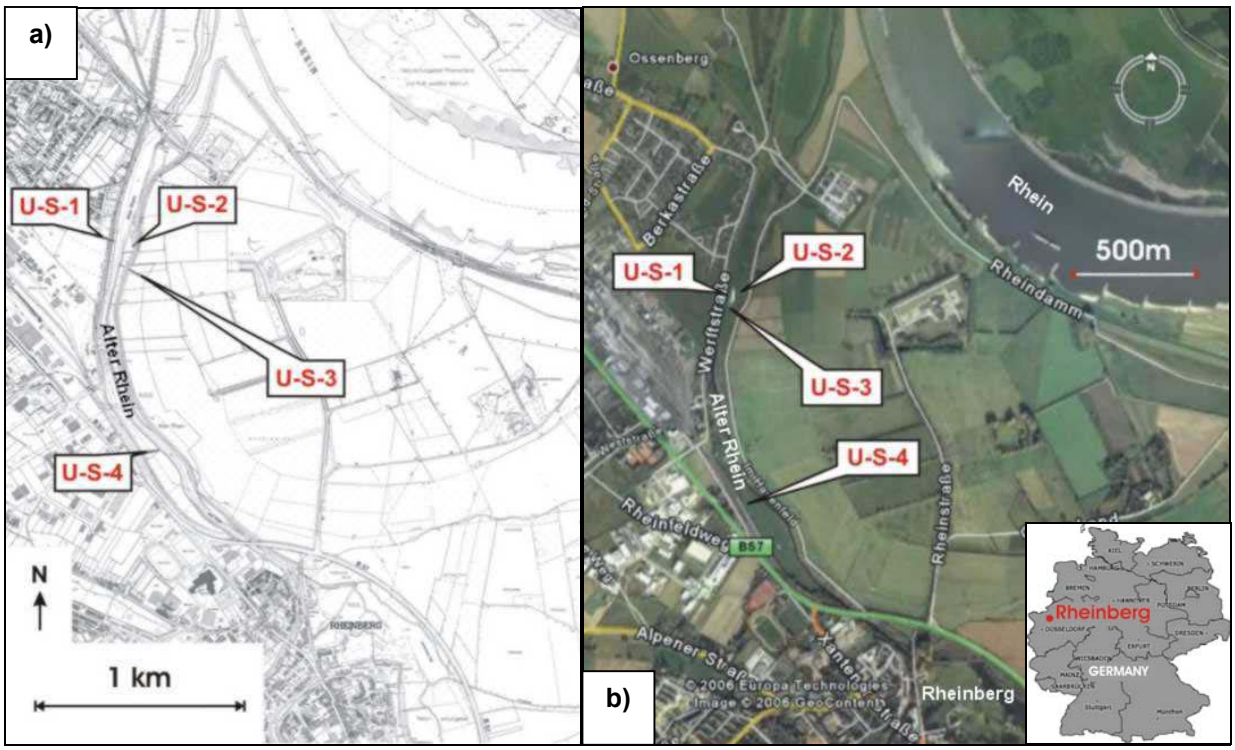

Fig 3-9: Locations of the sediments affected by hard coal mining: a) topographical map (based on DGK 5 G - NRW, exemplars 4405-10, -11, -16 and -17); b) aerial photograph (based on GLE, 2006); small map of Germany based on: http://urlaub-deutschland.de/thumbs/deutschland.gif.

3.6 Thorium compounds industry

Prior to the development of nuclear reactions, thorium was almost exclusively used for the production of gas mantles to enhance their glowing power, today this branch is of lower importance. Nowadays, the applications of thorium are widespread in chemical, electronic and engineering industries, commonly as an additive. It is an important substance in the development of atomic energy installations and also used in vacuum technology. Thoriated welding electrodes are produced for the "tungsten inert gas (TIG) welding" to aid arc ignition and stability, magnesium-thorium alloys are irreplaceable in jet-engines due to their hardness. (PENFOLD et al., 1999). This property was also the reason for its use as an additive in catalysts. In the optical industry, thorium fluorides are used for the anti-reflective coating of opto-electrical lenses, thorium containing polishing powders are used as well (DALHEIMER & HENRICHS, 1994, LANDROCK, 2002). Apart from those applications, research institutes use thorium compounds for chemical purposes (GELLERMANN et al., 2003).

Thorium is a substituting component of many minerals and those ones of commercial importance due to high thorium concentrations include monazite [(Ce, La, Nd, Th)PO_4], thorite [$ThSiO_4$] and thorianite [(Th, U)O_2]. It has chemical properties similar to those of uranium and some rare earth elements (PENFOLD et al., 1999, GRAUBNER, 1980).

Thorium is generally obtained by first concentrating the minerals, then the concentrates are decomposed by acids resulting in thorium salts. The latter are the starting material for the production of metallic thorium, thorium nitrate has been used additively in the production of gas mantles (PENFOLD et al., 1999).

For investigations, samples were provided from two different sites in Brandenburg, Germany: this is on the one hand the vicinity of a former gas mantle factory in the city of Oranienburg, which has been destroyed by an air-raid at the end of the Second World War and therefore, thorium having been stored for production was spread on a large area, on the other the residue of a thorium-cobalt catalyst having been disposed at a fallow land in Schwarzheide was available.

3.6.1 Contaminated soil from destroyed gas mantle factory

In Oranienburg, two different sites are of radiological relevance today (MLUV, 2002), because two factories having dealt with radioactive substances were destroyed during the US air-raid on 15th March 1945 (STULZ, 1973). The attacks resulted in natural radionuclide bearing dust, which was widely spread on the factories' vicinities and therefore, the soils of those areas can still be strongly contaminated. Beside the former gas mantle factory, another company undertook chemical extractions of both uranium and thorium from ores (NAGEL, 2002). According to GELLERMANN et al. (2003), a total mass of 1,000,000 tons of significantly contaminated material must be assumed for that company's area, which consist of raw materials such as monazite sands and residues from processing as well. The total amount of radiologically relevant material annually arising in Oranienburg is estimated at 3000 tons being equal to 2000m^3

due to excavation operations. From the soils contaminated by radionuclide bearing dust three samples were delivered.

In the general beginning of the production of incandescent gas mantles, an aqueous solution of Th-nitrate is applied onto tissues consisting of synthetic fibres (carrier substance) and then converted into Th-hydroxide by means of aqueous ammonia. The tissue is cut into quadratic cloths of different sizes in dependence of the mantle to be produced. Then, it is fixed onto a ceramic ring, oxidised to ThO_2 by incineration and finally coated protectively for transport. The whole process does not produce any volatile components. Today, there is only one manufacturer of thorium containing gas mantles in Germany, the production rate is of about 550,000 pieces per year. The annually needed amount of Th-nitrate is given by 500-600kg whereas the production volume of ThO_2 is roughly of 90kg. The latter is contained in dimensions of 0.03-0.36g in each mantle (LEOPOLD et al., 2002).

3.6.2 Catalyst-residue from FISCHER-TROPSCH-synthesis

At the site Schwarzheide, the chemical industry was founded in the 1930's by intention of producing synthetic fuels from the hydrogenation of brown coal, which is found in the Lausitz area close by (SCHULTE, 2005). This process was developed by the German chemists FRANZ FISCHER and HANS TROPSCH in 1923 and is therefore called "FISCHER-TROPSCH-synthesis" (FT-synthesis). Before the procedure is started, the coal is grinded. That powdered coal is then transferred into a synthesis gas generator of high temperature and pressure along with steam (fig. 3-10). According to FIESER & FIESER (1954), the hydrogen of the steam and the carbon oxides of the coal respond in forming water gas (mixture of carbon monoxide and hydrogen):

$$C + H_2O \rightarrow CO + H_2 \qquad \text{[equ. 7]}$$

The ashes from incinerating are removed and the water gas is purified from substances such as oxygen, sulphur and bitumen, which can damage the catalyst of the next step. The proper FT-synthesis takes place in a so-called "synthesis reactor" at temperatures of 160-350°C and pressures of 1-30bar. Due to the presence of the catalyst, which mainly consists of nickel, iron or cobalt and was formerly impured by 18% thorium for strength (FISCHER & MEYER, 1931), the water gas is forced to form long-chain hydrocarbons (FIESER & FIESER, 1954):

$$n * CO + 2n * H_2 \rightarrow C_nH_{n2} + n * H_2O \qquad \text{[equ. 8]}$$

$$n * CO + (2n+1) * H_2 \rightarrow C_nH_{2n+2} + n * H_2O \qquad \text{[equ. 9]}$$

The optimal ratio of CO and H_2 is of 1:2. Once started, the reactions are continuously performed and because those are of exothermal character, it is quite important to control the heat by an exchanger. Otherwise, the catalyst would be coked resulting in a reducing or blocking of the synthesis. Especially the temperatures are responsible for the types of fluid hydrocarbons being formed. High temperatures (> 330°C) result in shorter hydrocarbon chains such as petroleum whereas longer hydrocarbon chains like Diesel-fuel are created by lower temperatures (< 250°C).

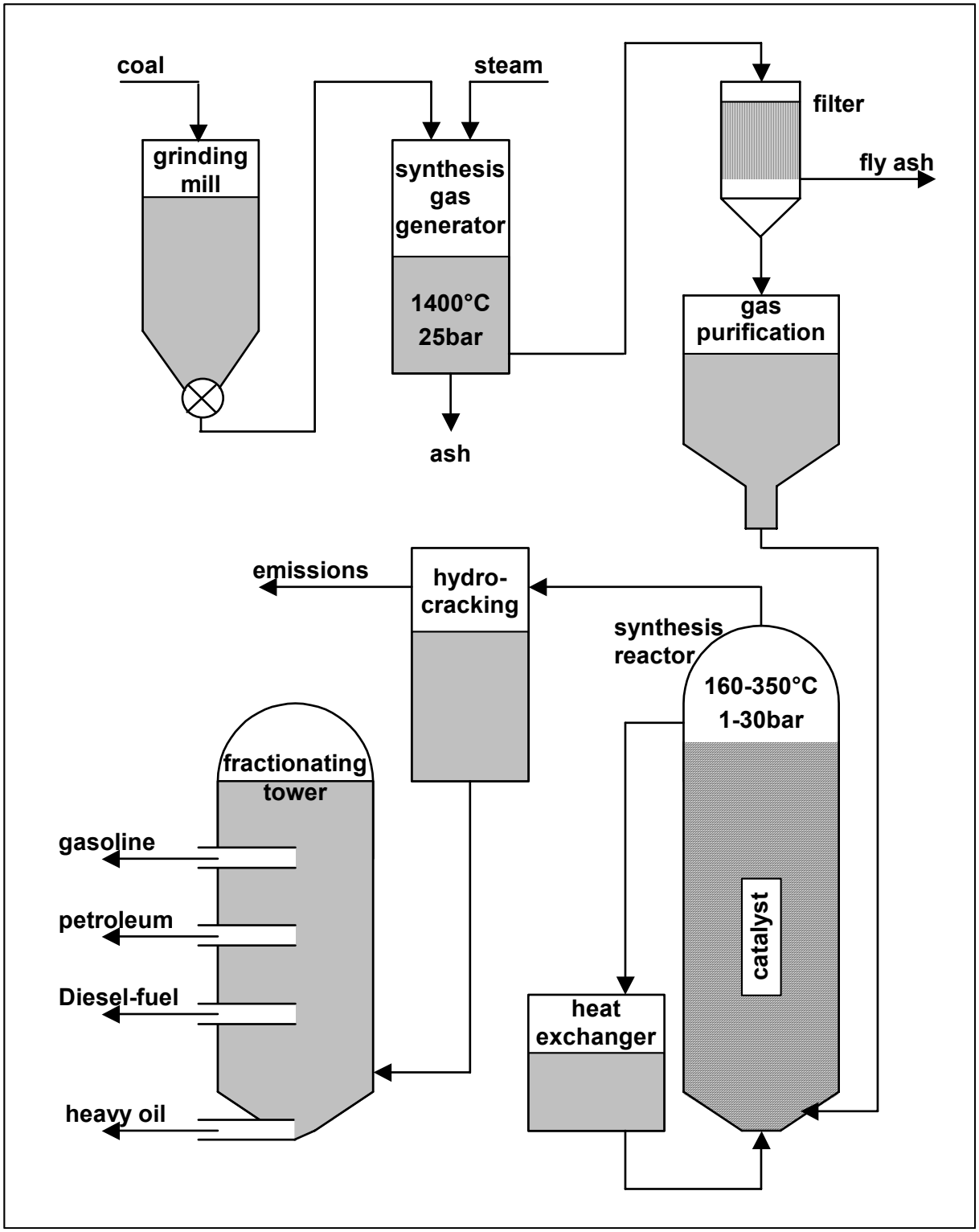

Fig. 3-10: FISCHER-TROPSCH-synthesis (based on FIESER & FIESER, 1954, CHRISTEN, 1976, VWU, 2005).

In frame of the FT-synthesis, beside fuels also lubricants and waxes are formed. After refining by cracking especially of the waxes into shorter hydrocarbon chains, the produced fuels are fractionated by density. The efficiency of the FT-synthesis is given by 1 ton of petroleum from 1.5-2 tons of coal. Nowadays, this kind of producing fuels is only applied in two countries worldwide due to relatively low costs of crude oil: in South-Africa and in Malaysia (FIESER & FIESER, 1954, CHRISTEN, 1976, VWU, 2005).

Today, in Schwarzheide the FT-synthesis is no longer practised, it was abandoned in the 1970's by the government of the GDR. In the 1990's, the residues from the processing have been removed and the area got decontaminated (FELDHEIM et al., 1995). Those residues mainly consisted of coal sludge and catalysts and lead to contaminations by PTB's, BTEX's or heavy metals as well (MLUV, 2005). The thorium-cobalt catalysts caused a significant thorium contamination of the soils (GELLERMANN et al., 2003), from which one sample was available.

3.6.3 Produced TENORM

The use of thorium for special purposes leads to enhanced activity concentrations of those products. According to table 3-7, especially thorium containing gas mantles can have activity concentrations up to some 10^6Bq/kg corresponding to a few thousands Bq per mantle piece. Data for the only German gas mantle factory show that those activities are then summarised up to 9MBq of $^{232}Th_{nat}$ per transport of 6000 gas mantles pieces (LEOPOLD et al., 2002). As mentioned by GELLERMANN et al., (2003), the German railway company still uses a certain amount of thorium gas mantles (2003: <100,000 pieces), but they are replaced step by step. Since the mantles are consumed by glowing (operation time of about half a year), they are easily crumbled during the replacing, which then generates thorium bearing dust to be collected by vacuum cleaners, whose filters can be of radiological relevance. Beside some optical lenses of high thorium concentrations, the other important thorium containing product are the thoriated welding electrodes made for tungsten inert gas welding. In frame of the welding process and abrading the electrodes, thorium bearing dust is generated, too. The longer the period between

Table 3-7: Activity concentrations of thoriated products (DALHEIMER & HENRICHS, 1994, GELLERMANN et al., 2003, LEOPOLD et al., 2002, PENFOLD et al., 1999).

material	activity concentration [Bq/kg]			
	^{232}Th	^{228}Ra	^{228}Th	^{230}Th
gas mantles	400 - 3,200,000	n.d.	n.d.	n.d.
	1000 - 4000 [Bq/piece]	n.d.	n.d.	n.d.
gas mantles used by German railway	1,800,000	1,050,000	850,000	500,000
	250 [Bq/piece]	150 [Bq/piece]	120 [Bq/piece]	70 [Bq/piece]
discharge lamps	100 - 1000 [Bq/piece]	n.d.	n.d.	n.d.
thorium fluorides	700 - 1600	n.d.	n.d.	n.d.
optical lenses	400,000	n.d.	n.d.	n.d.
TIG welding electrodes	27,000 - 160,000	n.d.	100,000	n.d.
	16,000 - 160,000 [Bq/piece]	n.d.	3000 - 32,000 [Bq/piece]	n.d.
alloys for jet engines	70,000	n.d.	n.d.	n.d.
colour pigments	50,000	n.d.	n.d.	n.d.

n.d.: no data available

Table 3-8: Mass classification by ^{232}Th activity concentration for annually excavated material from Oranienburg (according to GELLERMANN et al., 2003).

	^{232}Th activity concentration [Bq/kg]					total mass
	200 - 1000	1000 - 10,000	10,000 - 50,000	50,000 - 100,000	> 100,000	[t/a]
excavation material [t/a]	1500	900	450	150	< 10	3000
percentage	50%	30%	15%	5%		100%

the TIG welding electrodes' production and their final use, the higher are the activity concentrations of the growing progenies ^{228}Ra and consequently ^{228}Th (GELLERMANN et al., 2003).

On that special site in Oranienburg where uranium and thorium ores have been treated, some investigations were undertaken by GELLERMANN et al., (2003). For some hot spots within that area, ^{232}Th concentrations of more than 100,000Bq/kg had to be taken into consideration. GELLERMANN et al. (2003) gave also a rough mass classification by ^{232}Th activity concentration for amounts in whole Oranienburg, which had to be annually expected due to excavation operations (table 3-8). At the site Schwarzheide, huge amounts of thorium contaminated soils were caused by the presence of thorium-cobalt catalysts and their residues on a fallow land.

3.7 Uranium industry

Uranium is present in the Earth's crust at an average concentration of 3ppm (DAHLKAMP, 1993). This value differs in dependence of the type of rock the uranium is stored due its geological genesis, i.e. magmatic differentiation or metamorphosis for example. Acidic rocks such as granites being made of high silicate concentrations have generally higher uranium contents than basic or sedimentary rocks (chapter 2.2 Definitions of radioactive materials) (KEMSKI et al., 1996). But if enrichment processes like ascending uranium bearing waters (chapter 3.4.2 Produced TENORM) or sedimentary fractionating took place, the uranium concentrations can be significantly enhanced in rocks of usually low concentrations. From the commercial point of view, the most important uranium bearing mineral is uraninite [UO_2], which can be transferred from crystalline into colloidal structure (pitchblende) by weathering processes. Other common chemical variations found in nature are uranium trioxide [UO_3] and triuranium octaoxide [U_3O_8] (NICKEL, 1980). According to their geological genesis, uranium deposits can be classified into seven types (GATZWEILER & KEGEL, 1989):

1. Unconformity type

Cratonic Precambrian rock formations are closely connected to unconformities, which separate older Proterozoic metamorphic rocks from middle Proterozoic clastic sediments. The uraninite deposits occur as dykes or lenses and contain typically extremely high uranium concentrations of more than 1% U. Most important deposits are located in the Athabaska district, Canada, and in the Pine Creek formation, Australia.

2. Conglomerate type

Archaic and early Proterozoic quartzic conglomerates are mainly formed as seams, they show lower uranium contents up to 0.1%. Beside uraninite also gold and heavy minerals occur. Representative areas are the Witwatersrand region, South Africa, and the Elliot Lake district, Canada.

3. Sandstone type

Sandstones of mostly Phanerozoic age are evolved in cratonic inland basins. The deposits are formed as layers, lenses or linear shapes and can be of large dimensions. Uraninite is precipitated in the sandstone's pores or accumulated on clay minerals and results in uranium concentrations of 0.1-0.2%. This type of deposit is very common, such an important mining district is located in western USA and in Niger.

4. Dyke type

Dyke deposits are closely connected to granite bodies, where pitchblende occurs in the dykes and on related tectonic fracture zones. The uranium content is of 0.1-1% and the thickness of the ore bearing structures can reach more than 1m. Considerable deposits are known from the European Variscides, Port Radium, Canada or Colorado, USA.

5. Magmatic type

Due to their magmatic genesis, massive intrusive bodies such as granites, quartzic monzonites, pegmatites and carbonatites can be impregnated by uraninite and contain uranium concentrations up to 0.1%. A representative of this type is the deposit Rössing, Namibia.

6. Surface type

Porous carbonatic sediments close to the surface, mainly in aride climate regions, contain lenses of uranium ores being connected to shallow tributaries. This type is also called "Calcrete-type" and the main uranium mineral is the yellow coloured Carnotite in concentrations up to 0.1-0.2%. The most important Calcrete deposit is located in Yeelirrie, West Australia.

7. Undifferentiated types

Those deposits are mostly designed in dyke-style, sometimes characterised by an alteration of the dead rock by Na-metasomatism (albitite-type), others are connected to breccias (Olympic Dam, South Australia). Also the impregnation deposits consisting of black shales such as Ronneburg, Germany, are not clearly classified.

Uranium is mostly mined in open pits, whereas underground mining is usually done in case of magmatic bodies or dykes. Since uranium is often accompanied by other minerals of hydrothermal state such as copper, silver, gold, lead or nickel (MATTHES, 1996), uranium deposits are of highly commercial interest.

3.7.1 Extraction process

In general, the first wanted product from uranium ore is the so-called "yellow cake", which is the basis for further applications of both military and civil purposes (UIC, 2006). The processing scheme of producing yellow cake from the mined uranium ore is given in fig. 3-11. The uranium bearing rock is firstly crushed and milled down to a grain size of 20mm and less. By adding water a suspension is generated and after its thickening, it is filled into a leaching tank. There, the uranium is converted from the insoluble four-valent state into the well soluble six-

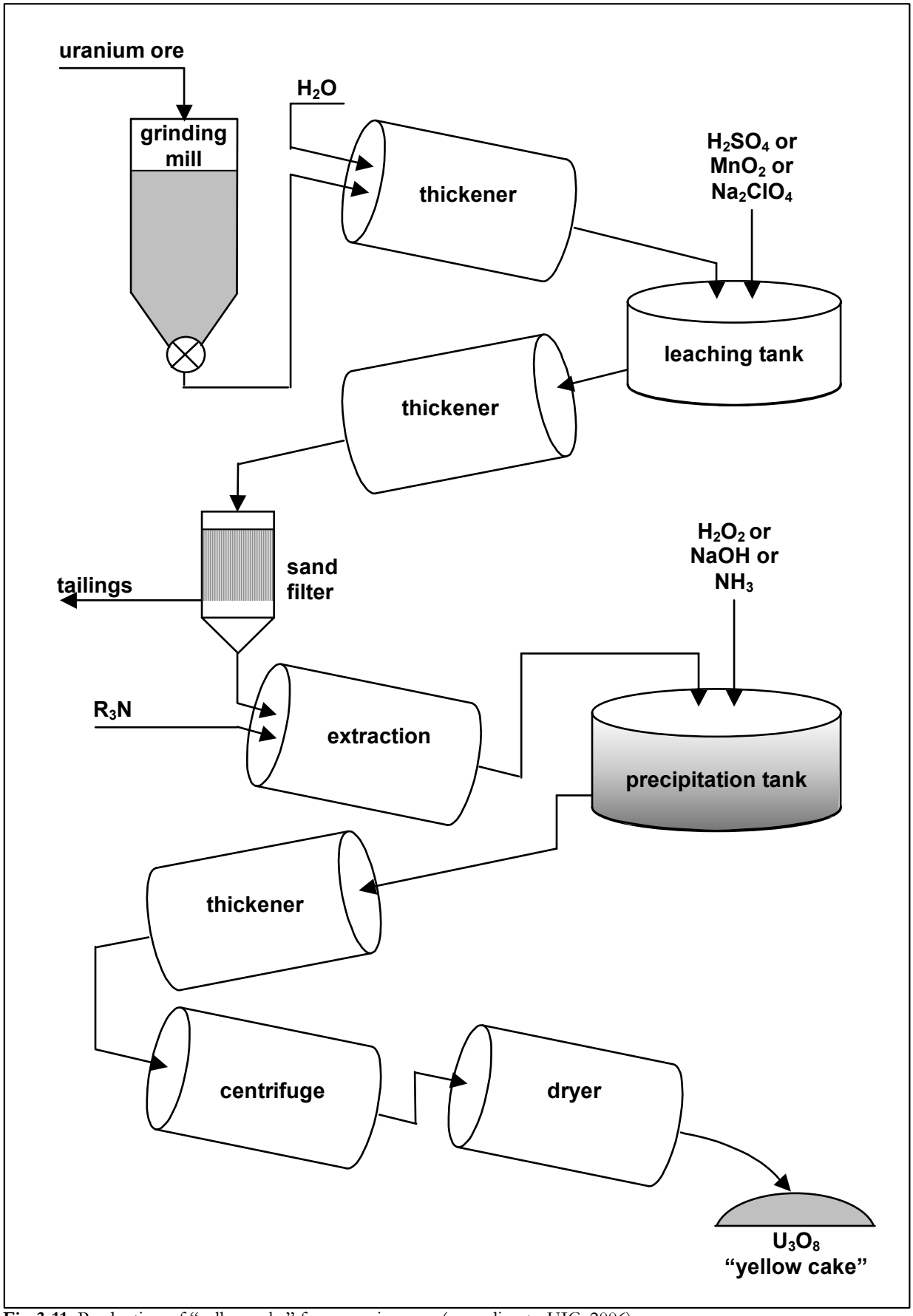

Fig 3-11: Production of "yellow cake" from uranium ore (according to UIC, 2006).

valent state by oxidation (GEI, 2006). As oxidising agents sulphuric acid [H_2SO_4], but also

manganese oxide [MnO_2] or sodium chloride oxide [Na_2ClO_4] can be used (SETTLE, 2005):

$$UO_3 + 2\ H^+ \rightarrow UO_2^{2+} + H_2O \qquad \text{[equ. 10]}$$

$$UO_2^{2+} + 3\ SO_4^{2-} \rightarrow UO_2(SO_4)_3^{4-} \qquad \text{[equ. 11]}$$

By doing so, the very most of the uranium is leached from the ore and transferred into the solution. After another thickening, the solid components, remnants of the initial ore, are removed by filtering and then allowed to settle out in a tailing pond. The dissolved uranium must be purified from other leached ingredients and further concentrated, which is undertaken by extraction. For that purpose, tertiary amines in an organic kerosene solvent are added to the sulphuric acid solution, the first reaction results in amine sulphate (SETTLE, 2005):

$$2\ R_3N + H_2SO_4 \rightarrow (R_3NH)_2SO_4 \qquad \text{[equ. 12]}$$

Secondly, the produced amine sulphate extracts the uranyl ions into organic phase while the impurities remain in the aqueous phase. In the case of the uranyl sulphate ion, the reaction is as follows:

$$(R_3NH)_2SO_4 + UO_2(SO_4)_3^{4-} \rightarrow (R_3NH)_4UO_2(SO_4)_3 + 2\ SO_4^{2-} \qquad \text{[equ. 13]}$$

Another way of extracting the uranium ions is given by ion exchange procedures. The solvents are then removed by evaporating in a vacuum (SETTLE, 2005). For neutralisation, hydrogen peroxide [H_2O_2], sodium hydroxide [NaOH] or ammonia [NH_3] are added. In running order, the resulting uranium bearing solids precipitate as either uranium peroxide [$UO_4 * UH_2O$], sodium diuranate [$Na_2U_2O_7$] or ammonium diuranate [$(NH_4)_2U_2O_7$]. After final steps of thickening, centrifuging and drying, the concentrate contains 70-90% of triuranium octaoxide [U_3O_8] and due to its yellow colour, it got the name yellow cake (GEI, 2006).

That triuranium octaoxide is the transportable medium of uranium, because its gamma dose rate is relatively low (in a distance of 1m from a transportation drum about half of that dose is received which occurs during a commercial jet flight by cosmic radiation) (UIC, 2006). Nuclear reactors demand for ^{235}U concentrations of 3.5-4% in the pellets while nuclear bombs need more than 90% of ^{235}U, the natural composition is of 0.7%. Therefore, the yellow cake is further processed at the destination sites for increasing the ^{235}U concentrations by converting it into gaseous uranium hexafluorides [UF_6], which is needed for the enrichment by gaseous diffusion. The resulting UF_6 is generated in two streams: one is increased in its percentage of ^{235}U [(highly) enriched uranium: (H)EU], the other is reduced in its ^{235}U concentration [depleted uranium: DU]. The latter fraction is usually stored or may be used for alloying ammunition. Pure uranium metal [U] is produced by reducing uranium tetrafluoride [UF_4], a by-product from the conversion into volatile state, with calcium or magnesium (SETTLE, 2005).

Table 3-9: Radiological data of uranium ores, dead rocks and tailings ([1]GATZWEILER, 1996, [2]MERKEL & DUDEL, 1998, [3]RÖNSCH, 1996, [4]ZAK et al., 2005).

material		U_{nat} content [%]	activity concentration [Bq/kg]		gamma dose rate [nSv/h]
			U_{nat}	^{226}Ra	
uranium ore mines[1]	$Australia_{olympic\ dam}$	0.07	18,000	n.d.	n.d.
	$Canada_{Mc\ Arthur\ river}$	15	3,810,000	n.d.	n.d.
	$Canada_{Rabbit\ lake}$	1	250,000	n.d.	n.d.
	$Namibia_{Rössing}$	2.2	560,000	n.d.	n.d.
	Niger	0.3	76,000	n.d.	n.d.
	Pribram (CZ)	0.4	102,000	n.d.	n.d.
	Ronneburg (D)	0.1	25,000	12,000	6000
	Schlema (D)	0.35	89,000	n.d.	n.d.
$dead\ rock_{without\ ore}$[3]		n.d.	n.d.	< 200 - 1000	< 200 - 500
$dead\ rock_{ore\ dispersed}$[3]		n.d.	n.d.	900 - 2000	500 - 1000
tailings[3]		n.d.	3500[2]	4000 - 15,000	2000 - 8000
		n.d.	n.d.	250 - 9000[4]	300 - 2000[4]

n.d.: no data available

3.7.2 Produced TENORM

During uranium mining and processing, tailings and dead rocks are the solid materials with high radionuclide concentrations beside the raw material itself (table 3-9). In case of undisturbed deposits, the uranium ore can be taken for being in secular equilibrium with progenies. The generated solid waste materials, especially the tailings, do contain a certain amount of the initial activity concentrations. In frame of the mining activities, rocks are mined having a too less uranium concentration for further processing and are so-called "dead rock", which are then heaped up in a stockpile close to the mine. But nevertheless, they can also show high radionuclide concentrations. In table 3-9, some important uranium deposits are listed. The "Mc Arthur River" mine, located in Canada, is that one with the highest uranium concentrations in the ore worldwide up to 15%, which corresponds to almost 4,000,000Bq/kg U_{nat}. For the tailings and dead rock stockpiles also some gamma dose rate measurements are available and show that especially the tailings emit high rates of gamma radiation. In case of the tailings special attention must be also paid, because they result from the treatment by sulphuric acid and are therefore acidified. According to BELEITES (1992), this is usually neutralised by lime, but if the uranium ore contained initially also sulphuric compounds such as pyrite, new sulphuric acid is continuously formed by rain fall. When that lime is used up, the acid's neutralisation is no longer enabled and leaching of heavy metals and radionuclides as well can occur.

3.7.3 Investigation sites

Solid materials resulting from uranium mining and processing were taken at two different sites due to access aspects. On the one hand rocks from stockpiles and sediments from tributaries crossing the mining area were collected in the uranium mining region of Pribram in the Czech Republic, on the other tailings were taken at a settling pond located close to Gorenja Vas, a small village in Slovenia.

Pribram (CZ)

In general, the Czech mining district of Pribram being located roughly 60km to the Southwest from the capital Prague is one with a long mining tradition and that is not based on uranium, but mainly on silver, lead and zinc beside some copper and tin deposits. According to HYRSL (1992), the historical roots can be traced back until the 14th century, when smelting works were officially mentioned for the very first time. All the ore bearing formations of Pribram are part of the main synclinal fold called "Barrandium" and can be characterised as classical dyke deposits, whose minerals are worldwide well known. The genesis of the ore beds is strongly connected to the Variscian intrusion of the Central Bohemian granite pluton and the resulting thermal metamorphosis and hydrothermal influence of older sedimentary layers (WALTER, 1995). Despite the fact that the uranium deposits of Pribram were already discovered in 1829, they became part of interest especially after the Second World War by intention of constructing nuclear weapons (HYRSL, 1992). The uranium bearing veins occur in the granite body and are mainly arranged in NW-SE-striking lineaments in turn of 90° towards the pressure direction, which formed the synclinal structure, and therefore they are due to extensive movements (WALTER, 1995). The exploitation was undertaken from 1945 until 30.09.1991 and during this period 100,000 tons of uranium ore are estimated to have been mined (HYRSL, 1992). The mining shafts reached a depth of almost 2km below the surface and more than 45km of galleries were installed and because all are connected, today this system is partly used for storage of natural gas, but the lowest floors are flooded by water (LACIOK, 2002).

In the mining area, six solid samples were collected, four rock samples taken from stockpiles and two sediments taken from riversides of tributaries crossing the mining area (fig. 3-12). The dark grey coloured samples U-ST-1 and U-ST-2 are derived from slag stockpiles, which are located in the Southwest, U-ST-3 is a pegmatite of light colour being collected at another stockpile in the North. U-ST-4 is a red coloured sandstone breccia of tectonic origin, which is partly interspersed by black pitchblende spheroids on the rock surface, it was found at the stockpile in the Northeast. All these hard rock samples are described in detail in the appendix, chapter "A-1 Material descriptions". The sediment samples represent both environmental conditions, the unaffected case and that one affected by mining activities. U-S-5 was taken at a tributary before it crosses the stockpile district, U-S-6 was collected under a road bridge from a sewer being fed by a tailing pond, the access to that pond was denied. The sample classification is given in chapter "4. Material preparation and examination methods".

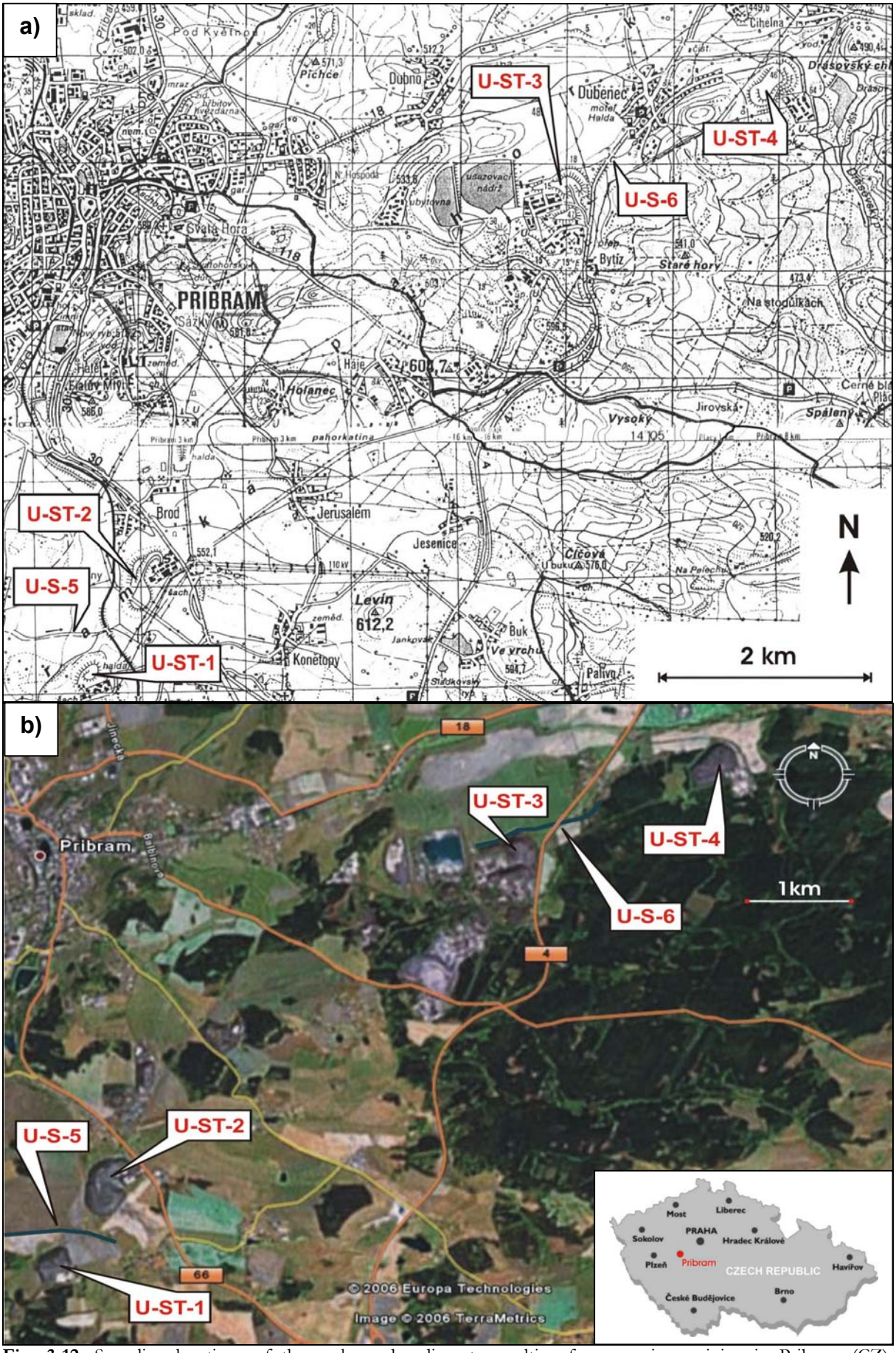

Fig. 3-12: Sampling locations of the rocks and sediments resulting from uranium mining in Pribram (CZ): a) topographical map (taken from LACIOK et al., 2002); b) aerial photograph (based on GLE, 2006); small map of Czech Republic based on: http://www.zeppelin.com/D/company/adressen/tschechien.html.

Gorenja Vas (SL)

In order to complete the series of radioactive materials arising in frame of uranium mining and processing, tailing samples were collected at a site in Western Slovenia. 35km to the West from the capital Ljubljana the village Gorenja Vas is located and in a near valley, an uranium ore deposit was discovered in 1960 (CADEZ et al., 2002). The mining activities started in 1982 and in 1984 the ore processing began, but due to economic reasons, the production was already ceased in 1990. Within those 6 years, 620,000 tons of ore were mined and the resulting waste materials, i.e. dead rocks and tailings, were disposed close by (fig. 3-13). The ore deposit is located in the Zirovski Vrh massif, which is part of the main geological structure called "Dinarides", and consists of partly double-S folded Carboniferous schists and Permian clastic strata laying on younger Triassic rocks, mainly dolomite (CADEZ et al., 2002). This layer arrangement was caused by overthrusting movements in frame of the early Alpidic Orogenesis of Jurassic age (SCHÖNENBERG & NEUGEBAUER, 1997). The Permian sandstones are of fluviatil origin and can be divided into the lower grey and the upper red formation. The diagenetic uranium mineralisation appears exclusively in the lower grey formation as lens shaped or belt elongated cement in the sandstones. The maximum thickness of the ore bearing zone is of 150m within that 400m thick lower Permian, the dominating uranium minerals are uraninite and coffinite (CADEZ et al., 2002).

The tailing disposal site was constructed in a distance of roundabout 500m from the ore processing plant at a relatively shallow hill slope (fig. 3-13a). The tailings were transported by trucks to that pond, which still contains 720,000 tons of settled waste material corresponding to a volume of 400,000m^3. The maximum thickness of the tailings is given by 10m and on top they are covered by a 10cm thick clay layer and geotextiles as well (JOVANOVIC, 2002). On the bottom, the disposal site is isolated from the bedrock by compacted layers of clay and equipped with a water collection system. But nevertheless, due to heavy rainfalls in November 1990 (maximum daily precipitation of 90l/m^2), the tailings body began to slide for a distance of 0.5m, which was aid by the presence of an older renewed thrust-plane below. After an additional drainage tunnel

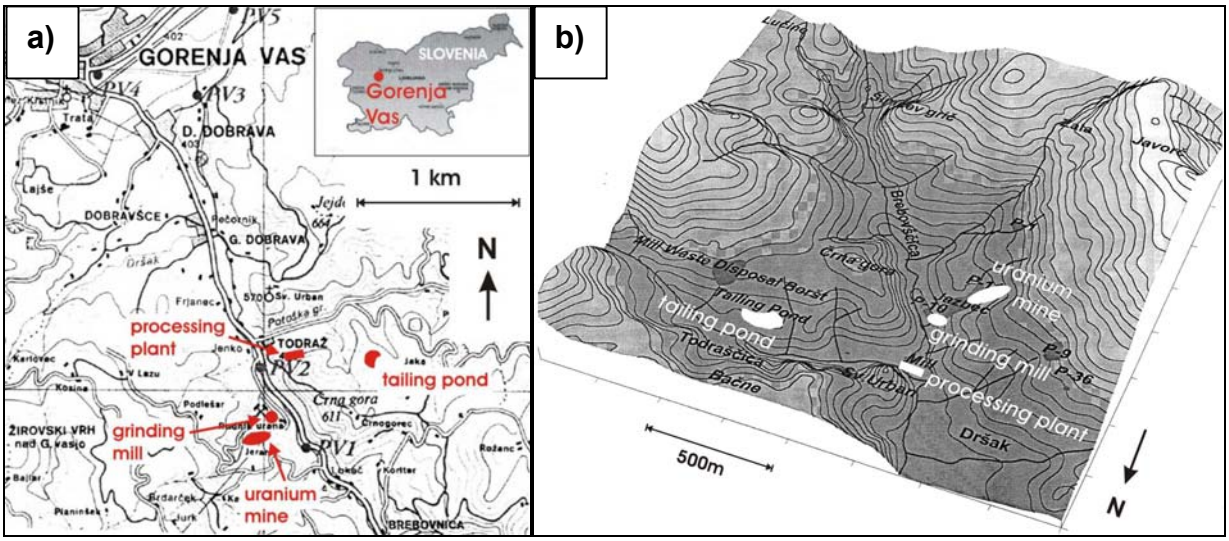

Fig. 3-13: Location of the Zirovski Vrh uranium mine: a) topographical map (based on http://www.rudnik-zv.si/NadaljnjiRazvoj.htm); b) three-dimensional map (based on BEGUS, 1989); small map of Slovenia based on http://www.rudnik-zv.si/images/ ZemljevidRZVvEvropi.jpg.

has been installed, the sliding movements stopped (BEGUS et al., 1996). Within that tailing pond four samples were collected. The disposed material was of homogenous consistence, because it was continuously light green coloured and of similar grain size <5mm. In addition, two hard rock samples (R-UO-1, R-UO-2) were taken from the lower Permian sandstone strata as raw material. A detailed description of them is given in the appendix, chapter "A-1 Material descriptions".

4 Material preparation and examination methods

The taken solid samples were investigated for their mobilisation potential of natural radionuclides, their radon emanation coefficients and the influence of the grain size for both parameters. For that purpose, a treatment scheme was developed as shown in fig. 4-1. Each single step is explained in the following chapters.

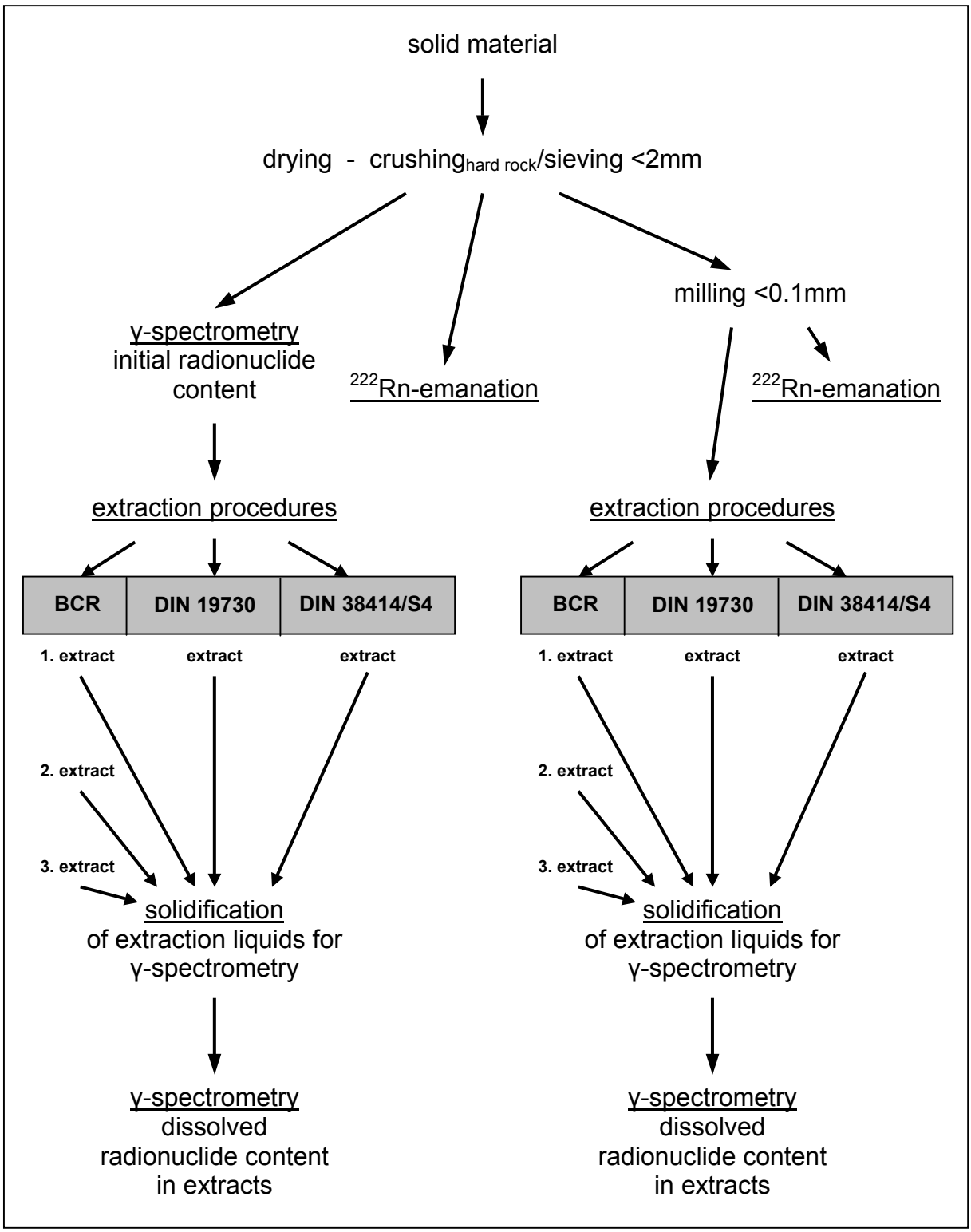

Fig. 4-1: Sample treatment scheme.

The taken TENORM-samples were classified according to their position in the processing scheme of the respective type of industry as described in chapter "2.3.2 Types of materials concerned", their exact determination and finally they were numbered. Therefore, each sample name consists of three positions, which are explained in table 4-1:

Table 4-1: Sample name classification.

position 1 position in processing scheme	**position 2** determination	**position 3** numbering
R = raw material **W** = waste material **U** = unwanted by-product **P** = product	**AO** = aluminium ore **F** = fertiliser **FD** = filter dust **FZM** = fused zirconia mullite **PG** = phosphogypsum **PO** = phosphate ore **RS** = red sludge **S** = sediment **SC** = scale **SL** = sludge **SO** = soil **ST** = stockpile **T** = tailing **UO** = uranium ore **ZS** = zircon sand	number

example: R-UO-2 means the second exemplar of the raw material sample uranium ore.

4.1 Material preparation

The solid materials were dried for 24h at 105°C, hard rocks were completely crushed for <2mm by a jaw crusher before. Then, the samples were sieved for the fraction <2mm, from which a portion was grinded for the fine milled fraction <0.1mm by a tungsten-carbide mill using an oscillating panel (made by HERZOG-company, type HSM 100 H). By doing so, potential wood and skeleton fractions in the solids were removed and two homogenous representants of the initial sample were obtained. In order to reduce the still inhomogeneous characteristics of the hard rocks' crushed fractions (<2mm), those were then milled to <0.1mm, so a proper material mixture was ensured.

The treated samples were simultaneously prepared for the measurement of their initial radionuclide content by gamma-spectrometry, determination of their radon emanation coefficient and three different extraction procedures.

4.2 Extraction procedures

In order to evaluate the availability of natural radionuclides in TENORM, three different extraction procedures according to international and German standards were applied for investigating the most important chemical types of bounding and transfer pathways. The 3-step extraction procedure proposed by the BCR ("**B**ureau **C**ommunautaire de **R**éférence", now "European Standards, Measurements and Testing Programme, SM&T") of the European Union provides extraction liquids being representative for the easily exchangeable, the reducible and oxidisable fraction. The leaching procedures according to the German standards called "DIN 19730" and "DIN 38414/S4" result in plant available respectively water soluble fractions.

In the beginning of each extraction procedure, the needed amount of dried material, which varies between the standard types, was exactly weighted and then filled in acid cleaned 250ml propylene (PP) centrifugal cups. By the (successive) adding of several reagents, the radionuclides of different types of bounding were solved in those liquids. For the preparation of the chemical solutions needed, always bi-distilled water and chemical solutions of the purification degree "p.a." were used. All the three procedures demand for extraction shaking, which was done by an overhead-shaker at 50rpm in accordance to the time limits mentioned in the respective standard instruction. After each step, the suspension in the PP-cup was centrifuged at 4500rpm for 5min, in some cases that centrifuging time was extended to 20min when the suspension was not fixed on the bottom of the cup before. The separated extraction liquid was then decanted by a 45µm membrane filter and transferred into an acid cleaned polyethylene (PE) storage cup of 250ml volume. In frame of the BCR procedure, the reagent of the next step was filled in the same PP-cup, which contained the remaining solid material on the bottom from the extraction step before.

4.2.1 Extraction according to BCR-approach

The BCR extraction procedure was carried out according to URE et al. (1993). This 3-step leaching test leads to three fractions, which were then measured by gamma-spectrometry for their content of natural radionuclides (fig. 4-2):

1. **easily exchangeable fraction**
   acid soluble, leaching of carbonates
2. **reducible fraction**
   leaching of amorphous manganese and iron oxides
3. **oxidisable fraction**
   leaching of organic matter and sulphides

As described in the official BCR extraction instruction, especially low pH-values and small ratios of reagent-solid (E1 and E2: 40ml-1g, E3: 50ml-1g) were chosen in order to minimise re-adsorption and precipitation reactions. But instead of a starting material's amount of 1g as proposed in the BCR-scheme, 5g were taken to ensure reliable measurements of the extracts by gamma-spectrometry later on. The time for the extraction by overhead-shaker was set to 24h for establishing leaching equilibrium.

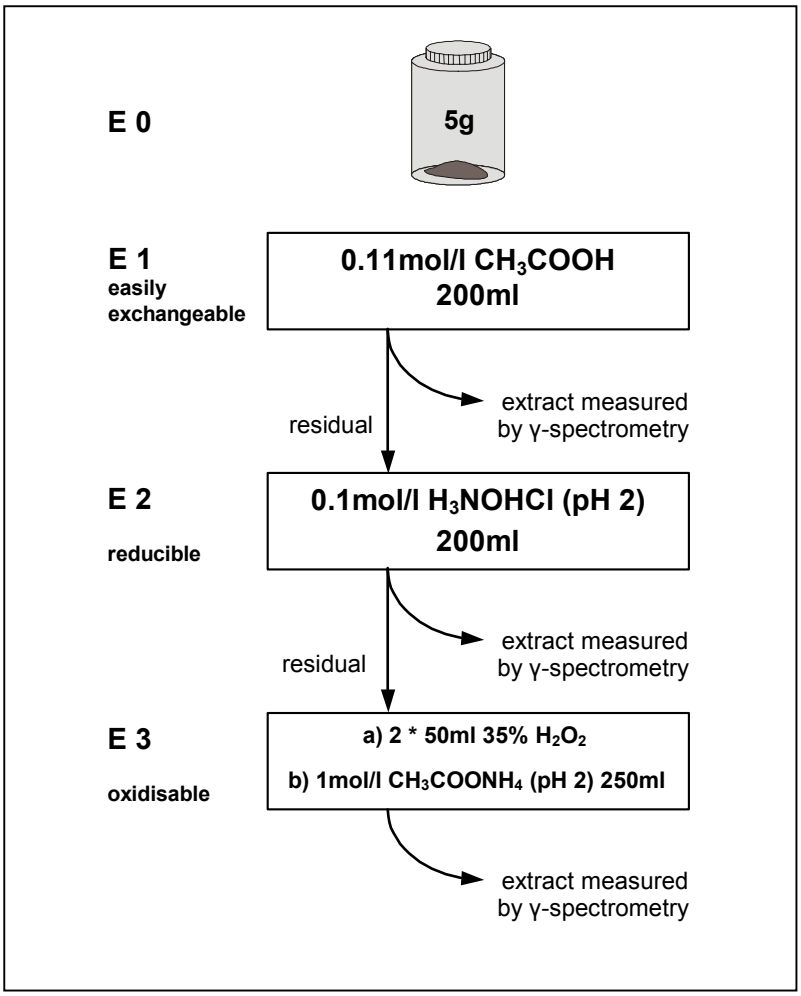

Fig. 4-2: Extraction scheme according to BCR-approach (illustration based on SULKOWSKI, 2002).

The extraction procedure was carried out as follows (fig. 4-2): a weighted mass of dried solid material was filled into a centrifugal cup (E 0) and 3 chemical reagents were added step-by-step. The procedure began for the easily exchangeable fraction by adding 200ml of acetic acid of 0.11mol/l (E 1). An equal suspension was ensured by a first manual shaking and then the centrifugal cup was shaken by overhead-shaker, so the solid material was always kept in suspension during extraction. After the removal of the liquid by centrifuging, this was followed by extracting the reducible fraction, which was obtained by using 200ml of 0.1mol/l hydroxylamine chloride adjusted to pH 2 by nitric acid (E 2). The liquid of E 2 was removed and the residual transferred into a glass cylinder. The oxidisable fraction started with adding 50ml of 35% hydrogen peroxide into that glass cylinder, which then was heated to near dryness in a sand bath of 200°C by roughly 1h (E 3a). After repeating that procedure and retransferring the remaining material into the initial centrifugal cup, 250ml of 1mol/l ammonium acetate was added, the pH adjusted to 2 by nitric acid (E 3b). After this last extraction step the residual was discarded (see chapter "4.3.1 High resolution gamma-spectrometry").

4.2.2 Extraction according to DIN 19730

The extraction procedure was carried out in accordance to DIN 19730 (1997) and results in the plant available fraction, which was then measured by gamma-spectrometry. The ratio of reagent-solid is given by 2.5ml-1g and means significantly low mechanical stress in frame of the extraction. The procedure was undertaken by filling 80g of dried solid material into a centrifugal cup and adding 200ml of 1mol/l ammonium nitrate [NH_4NO_3]. An equal suspension was ensured by a first manual shaking and then the centrifugal cup was shaken by overhead-shaker, so the solid material was always kept in suspension during extraction. The shaking time was fixed at 2h and then the reagent was removed by centrifuging and decanting to be stored in a PE-cup. The residual was discarded (see chapter "4.3.1 High resolution gamma-spectrometry").

4.2.3 Extraction according to DIN 38414/S4

In order to evaluate the water soluble fraction of natural radionuclides, the extraction procedure according to DIN 38414/S4 (1984) was applied. It is an commonly used approach for investigating the pollution potential of waters e.g. by muddy materials and its ratio of reagent-solid is of 10ml-1g for simulating realistic dissolving behaviour. 20g of dried solid material was filled in a centrifugal cup and 200ml of bi-distilled water was added. After a first manual shaking an equal suspension was ensured and the PP-cup was shaken for 24h of extraction time. The reagent was then removed by centrifuging and decanting to be stored in a PE-cup. The residual was discarded (see chapter "4.3.1 High resolution gamma-spectrometry").

4.2.4 Solidification of extraction liquids

Before the reagents were measured by gamma-spectrometry they were solidified. By doing so, a precipitation of particles on the bottom of the MARINELLI-beaker and therefore a wrong radionuclide activity concentration determination is avoided. This procedure was done as follows: after the extraction liquid's volume has been exactly determined, it's pH was adjusted to 7 by adding NaOH (7 is the pH value that Agar-Agar solidifies), 25g/l of Agar-Agar was added whilst stirring and then transferred into a MARINELLI-beaker. That cup was put in boiling water for at least 10min. This is necessary to destroy the Agar-Agar chains so that no precipitation, either of Agar-Agar or of contained particles, will occur when the cup is allowed to cool. In each MARINELLI-beaker, which had been constructed on purpose for volumes up to 250ml, the liquid level was adjusted for a constant height using bi-distilled water, so that the coaxial detector of the gamma-spectrometry was surrounded equidistantly at top and sides by solution in frame of all liquids' measurements. For the calculation of the activity concentration later on, the reagents' volume determined before was used.

4.3 Gamma-ray spectrometry

4.3.1 High resolution gamma-spectrometer system

For the detailed and reliable determination of natural radionuclides in solid materials and liquids as well, a high resolution gamma-spectrometer, which is installed at the Geology department of the Institute of Geography, University Duisburg-Essen, was used (MURRAY et al., 1987). The centre of this system is a negative poled (n-type), intrinsic **H**igh **P**urity **Ge**rmanium (HPGe) crystal of quasi-coaxial shape (type: NIGC 44; 65mm length and 50.4mm diameter) made by PRINCETON GAMMA-TECH™. Since that detector is additionally equipped with a beryllium entrance window, which is of almost 5cm diameter and fixed outside in a distance of 5mm to the detector, the minimum measurable gamma energy is reduced to 15keV. The germanium detector supplied with a preamplifier is permanently cooled by nitrogen and always kept under constant high-voltage of 4kV. The cylindrical lead cover in a size of approximate 0.5m height and 0.45m diameter provides shielding against cosmic background radiation. The samples can be put from above into that vessel respective on the detector when the lid is opened by a tackle. The system is adjusted to a detection limit of 1Bq/kg ^{226}Ra, a further description is given in the appendix, chapter "A-2-a Gamma-spectrometer".

The measurement method of a gamma-spectrometry system is based on the detection of the emitted photons by interaction with matter and their transformation into electrical impulses, which are then amplified. The most important physical processes occurring within the detector are the photo-effect (wanted due to complete energy transformation), COMPTON-effect (unwanted due to incomplete energy transformation) and electron pair formation (creates annihilation-peak at 511keV). The height of an impulse depends on the energy of the detected photon. An electrical unit called "Multi Channel Analyser" (MCA) sorts the impulses by height into different channels and stores the number of impulses for each channel, which are summed up at the end of measuring time. The result is an impulse-height-spectrum separated by channels, in which the number of impulses is proportional to the activity of the radionuclide emitting that special photon after the background was subtracted. The gamma spectra obtained by the system described above cover the energy range 15-2000keV. The number of channels classifies a gamma-spectrometry system for its exactness, the used MCA provides 8192 (2^{13}) channels per 2000keV and therefore, an energy range of 1keV is covered by more than 4 channels.

In frame of this thesis, natural radionuclides of both the ^{238}U and the ^{232}Th decay chain are in focus whilst ^{40}K turns out of any consideration due to its all-time presence. The radionuclides of relevance are summarised in table 4-2. All the mentioned elements are solid under environmental conditions, which means without any artificial treatment e.g. heating. But not all of them can be measured by gamma-spectrometry. ^{238}U and ^{228}Ra do not emit any gamma line whereas that of ^{228}Th is too weak for exact determination due to a very low emission probability of roughly 1%. ^{226}Ra has one characteristic gamma line at 186keV indeed, but that is easily disturbed when ^{235}U is present, too, because that emits an interfering photon energy at 185keV. Nevertheless, those radionuclides can be exactly determined by their progenies when radioactive equilibriums were

Table 4-2: Relevant radionuclides, analysed ones marked by * (according to SCHÖTZIG & SCHRADER, 2000).

radionuclide	half-life	strongest γ-line(s)	
		emitted at energy [keV]	yield per decay [%]
^{208}Tl*	3.1min	583.19	84.5
		860.56	12.4
^{210}Pb*	22.3a	46.32	4.2
^{214}Bi*	19.9min	609.31	46.1
		1120.29	15.1
^{214}Pb*	26.8min	295.22	19.3
		351.93	37.6
^{226}Ra	1600a	186.1	3.5
^{228}Th	1.9a	84.37	1.2
^{228}Ac*	6.15h	911.60	25.8
		969.11	15.8
^{228}Ra	5.8a	no γ-line	
^{234}Th*	24.1d	63.28	4.1
^{238}U	4.5 * 10^9a	no γ-line	

white: radionuclides of the ^{238}U decay series
grey coloured: radionuclides of the ^{232}Th decay series

established after 6 times of all passing progenies' half-lives roughly (FUNKE & SCHULZ, 1999, SCHKADE et al., 1999):

^{238}U: by ^{234}Th, after a storage period of 80 days
^{226}Ra: by ^{214}Pb and ^{214}Bi, after a storage period of 3 weeks
^{228}Ra: by ^{228}Ac, after a storage period of 36 hours
^{228}Th: by ^{208}Tl, after a storage period of 3 weeks, corrected for branching ratio of 33%

That means, the waiting period until a sample can be simultaneously measured for all those radionuclides amounts 80 days, because the longest time for establishing radioactive equilibrium is given by ^{234}Th. In order to avoid loss of the gaseous progenies ^{222}Rn and ^{220}Rn, the sample boxes (60ml boxes and MARINELLI-beakers of 250ml, 500ml and 1000ml volumes) were sealed by radon rejecting tape. Results of a density test of the 250ml MARINELLI-beakers introduced on purpose for the extraction liquids are presented in chapter "4.3.3 Radon-density control of 250ml MARINELLI-beakers", the other measuring geometries were proven radon dense some years ago. The absolute minimum amount of solid material for reliable measurements is given by 60g, which was then measured for at least 86,400s (1 day). The MARINELLI-beakers were measured for a few hours depending on the respective volume. Since the remaining material's volume of the solid residual fraction after the extraction procedures was much too small for reliable measurements by gamma-spectrometry (especially of the BCR), its radionuclide content was calculated by summing up the radionuclide concentrations of all extraction fractions and subtracting that value from the

initial radionuclide content. This approach is in accordance with SCHMIDT (2001) and ROSENBAUM-MERTENS (2003).

The measurements of solid samples were generally undertaken according to the German standard DIN 38414, part 16 (1988) "Determination of radionuclides in sludge, sediment and suspension by gamma-spectrometry", the extraction liquids were measured according to DIN 38404 C16 (1989) "Determination of radionuclides in drinking, ground, surface and waste water by gamma-spectrometry".

4.3.2 Correction of ^{234}Th and ^{210}Pb for self-absorption

The radionuclides ^{234}Th and ^{210}Pb emit one detectable gamma line each, but they are of low energy (table 4-2). In general, correction factors must be calculated for the detected number of impulses respectively activity concentration in the energy range <100keV due to absorption processes of photons within solid sample media. Gamma energy lines >100keV are also affected indeed, but their absorption dimension is negligible (RUCKERBAUER et al., 1997). In order to calculate the absorption coefficient, the method for cylindrical measuring geometries according to CUTSHALL et al. (1982) was applied. In frame of that approach, a gamma emitting point source was put centrally for the same time onto a calibration sample (A) of known composition and density and then onto the sample to be defined (B), each filled in a 60ml cylindrical box. In both cases, the count rate of the point source is determined and the correction factor for self-absorption "c_{sa}" can be calculated as follows:

$$c_{sa} = \frac{\ln\left(\frac{R_B}{R_A}\right)}{\frac{R_B}{R_A} - 1} \qquad \text{[equ. 14]}$$

R_A: count rate of calibration sample
R_B: count rate of sample to be defined

Since the dimension of self-absorption depends on the respective gamma energy, the correction factor must be calculated for some representative energies. For the corrections of ^{234}Th and ^{210}Pb, a ^{152}Eu/^{241}Am containing point source ("NP 363", made by ISOTRAK™) emitting gamma lines at 40keV, 45keV and 60keV was chosen, the measuring time set to 180s. A description of the point source as well as the obtained absorption coefficients for each solid sample are listed in the appendix, chapter "A-2-c Correction of ^{234}Th and ^{210}Pb for self-absorption".

4.3.3 Radon impermeability control of 250ml MARINELLI-beakers

The 250ml measuring geometry was introduced on purpose for the liquid volumes obtained from extraction procedures. Since the radon density of the used MARINELLI-beakers is inevitable for the exact determinations of ^{226}Ra and ^{228}Th, it was proven by the use of milled, strong

radiating uranium ore. Such a MARINELLI-beaker was completely filled by that raw material, sealed and then put into a bigger radon dense vessel containing aged and therefore radon free air to be stored for 3 weeks. That vessel was equipped with two valves, so the air inside could be easily transferred into the radon monitor RAD7 made by NITON™ when the storage period passed by. After the determination of ^{222}Rn in the air surrounding the MARINELLI-beaker, the air inside the beaker was almost completely transferred into a LUCAS-cell and then also measured for ^{222}Rn by the scintillation counter LUK 4E made by RADON V.O.S.™. By doing so, the ^{222}Rn concentration in the air inside the MARINELLI-beaker was given by 33,390Bq/m^3 whereas the air outside the beaker showed a ^{222}Rn concentration of 31.6Bq/m^3. That means in consequence that the radon loss resulting from the sealed 250ml MARINELLI-beaker is lower than 0.1%, which is an acceptable dimension. A description of both radon measuring devices is given in the appendix, chapter "A-2-d Radon measuring devices".

4.3.4 Calibration of 250ml geometry for liquids

A gamma-spectrometer must be calibrated for efficiencies and backgrounds of the used measuring geometries each. That system described above is calibrated for the 60ml boxes, 500ml and 1000ml MARINELLI-beakers for a long time and regularly proven by participations in intercomparison measurements. The special 250ml measuring geometry introduced for the extraction liquids was calibrated by a mixture of an intercomparison waste water sample bearing several artificial radionuclides, which has been proven true by more than 280 individual measurements, and an ^{241}Am containing calibration liquid for the low energy area, both provided by BfS. The exact radionuclide content and the respective activity concentrations are listed in the appendix, chapter "A-2-b Calibration liquid". That liquid mixture was solidified in the same way as the extraction liquids were (chapter "4.2.4 Solidification of extraction liquids"), the volume having been exactly fixed at 250ml. A gamma spectrum was then acquired by a measuring time of 8h (fig. 4-3 above). This period was chosen to establish background and peak shapes similar to those of the spectra obtained by the extraction samples, so they are comparable in style and dimension. Based on that spectrum, an efficiency curve was calculated covering the energy range 15-1500keV (fig. 4-3 below). The green error ranges of the radionuclides are not located on the same energy position as in the gamma spectrum, because the calculation of the curve demands for an interpolation of the obtained efficiency by each peak and by doing so, the curve's shape is adjusted. The trend of the efficiency curve is developed in that style as it is typical for coaxial shaped HPGe-detectors: a strong efficiency increase with the maximum at an energy of roughly 100keV and then an immediate turning into shallow decreasing. The detection limit of this calibration is given by 0.5Bq/l for ^{226}Ra. The background of this measuring geometry was determined by measuring an empty 250ml MARINELLI-beaker 5 times longer than a conventional measuring period of 86,400s, this period was finally extended up to 7 days.

4.3.5 Quality assurance of the 250ml calibration

In order to prove the established calibration for 250ml extraction liquids true, an intercomparison measurement was arranged with the "Laboratory of Radiometry" of the Polish

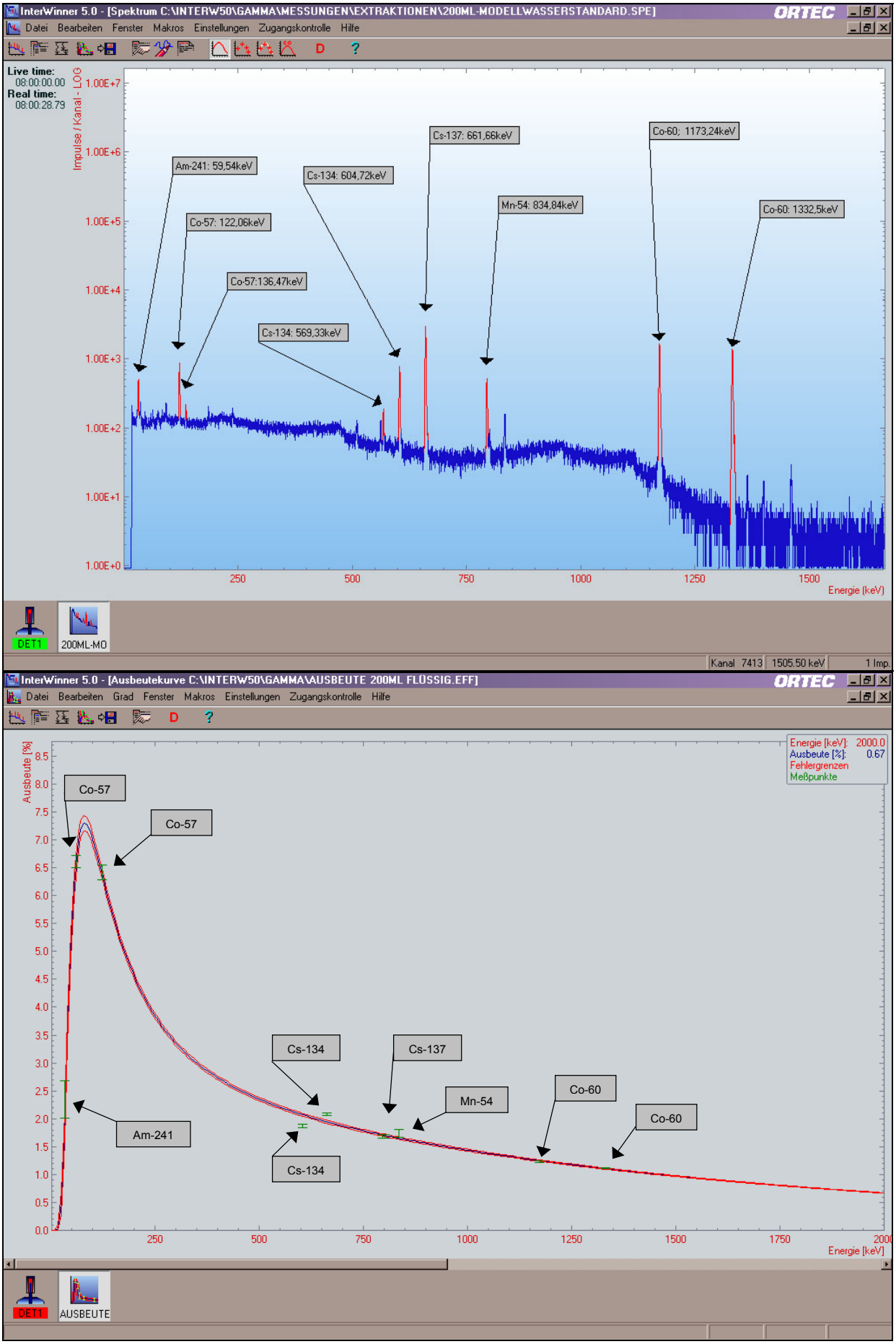

Fig 4-3: above: gamma-spectrum acquired from the calibration liquid mixture; below: efficiency curve calculated from the spectrum above.

Table 4-3: Activity concentrations of the 250ml calibration mixture measured by University Duisburg-Essen and Polish Central Mining Institute, GIG, compared with BfS-certificate.

radio-nuclide	activity concentration [Bq/l]			relative uncertainty [%]		absolute uncertainty [Bq/l]	
	Essen	GIG	BfS-certificate	Essen [2σ]	GIG [1σ]	Essen [2σ]	GIG [1σ]
^{54}Mn	9.4	n.d.	9.1	7.4	n.d.	0.7	n.d.
^{57}Co	12.1	12	11.95	4.0	20	0.5	2.4
^{60}Co	204	208	205	2.3	5	4.7	10.5
^{134}Cs	44.3	50.2	47.4	3.0	4.2	1.3	2.1
^{137}Cs	229	203	214	2.8	4.3	6.5	8.7
^{241}Am	175	173	173	6.1	3.1	10.6	5.4

n.d.: not determined

Central Mining Institute (GIG, Dr. Boguslaw Michalik), Katowice. The same calibration standard was measured there for the same period on an equal detector (n-type HPGe of same shape with carbon-epoxy window), which was calibrated for a similar measuring geometry of 100ml. The obtained results are presented in table 4-3 and show well correspondences for all radionuclides. These results are again in best agreement with those concentrations having been certificated for the calibration liquids by BfS, that certificate is given in detail in appendix, chapter "A-2-b Calibration liquid". That means in further consequences that there is no mentionable influence by the slightly different calibration volumes of both Essen and GIG laboratories.

4.3.6 Relation of liquid and solid activity concentration

To determine the radionuclide concentrations dissolved in each extractant as a proportion of the starting solid material, it is necessary to calculate the volume activity concentration of the extraction liquids as compared to the activity concentration in the dry mass. That is possible because the amount of starting material is weighed carefully before the extraction is undertaken. Therefore, each extraction liquid activity represents a percentage of activity concentration of the starting material's dry mass activity concentration. The relationship between the activity concentration of the liquid (i.e. $activity_{liquid}$) and the dry mass (i.e. $activity_{solid}$) is given by the following equation:

$$activity_{solid}[Bq/kg] = \frac{1000}{\frac{1000}{vol_{liquid}[ml]} \cdot weight_{materialextracted}[g]} \cdot activity_{liquid}[Bq/l] \quad \text{[equ. 15]}$$

factor for correlation of extraction liquid given in [ml] up to 1 l

factor for correlation of volume extraction liquid up to weighted amount of material given in [g] filled in centrifugal cups and relation to 1 kg

4.4 Radon emanation

Beside the initial radionuclides' activity concentration analysed by gamma-spectrometry and their type of bounding obtained by the extraction procedures, the radon emanation coefficient was determined for each solid sample. For that purpose, a well defined procedure having been developed by WIEGAND (1999) in the Geology department of the University Duisburg-Essen was applied (fig. 4-4). In the beginning, material was filled into a polypropylene cup of 1175ml volume, which acts as an emanation chamber, up to an exact height of 1cm and then the weight of the needed amount of material was determined. After radon dense sealing, the chamber was stored for 3 weeks to let establish the radioactive equilibrium between ^{226}Ra and its progenies. Due to the fact that the chamber was equipped with two valves, an easy transfer of the air bearing regenerated ^{222}Rn into a 600ml LUCAS-cell, which contained aged air, was enabled when that period passed by. For that transfer within a closed circular, the volume of the LUCAS-cell was two times changed with that one of the emanation chamber by using a manual pump. The filled LUCAS-cells were stored for 3.5h to let establish the radioactive equilibrium between ^{222}Rn and its progenies and after that period passed by, the cells were measured by the scintillation counter LUK 4E made by RADON V.O.S.™ (see chapter "4.4.1 600ml LUCAS-cells"). For the calculation of the emanation rate, a reduced radon concentration compared with the situation before the transfer must be taken into account:

- the radon bearing air in the chamber is diluted by the volume of the LUCAS-cell inclusive the connected tubes
- the air volume of the chamber is reduced from 1175ml to 1090ml due to the contained amount of solid material (usually 85ml)

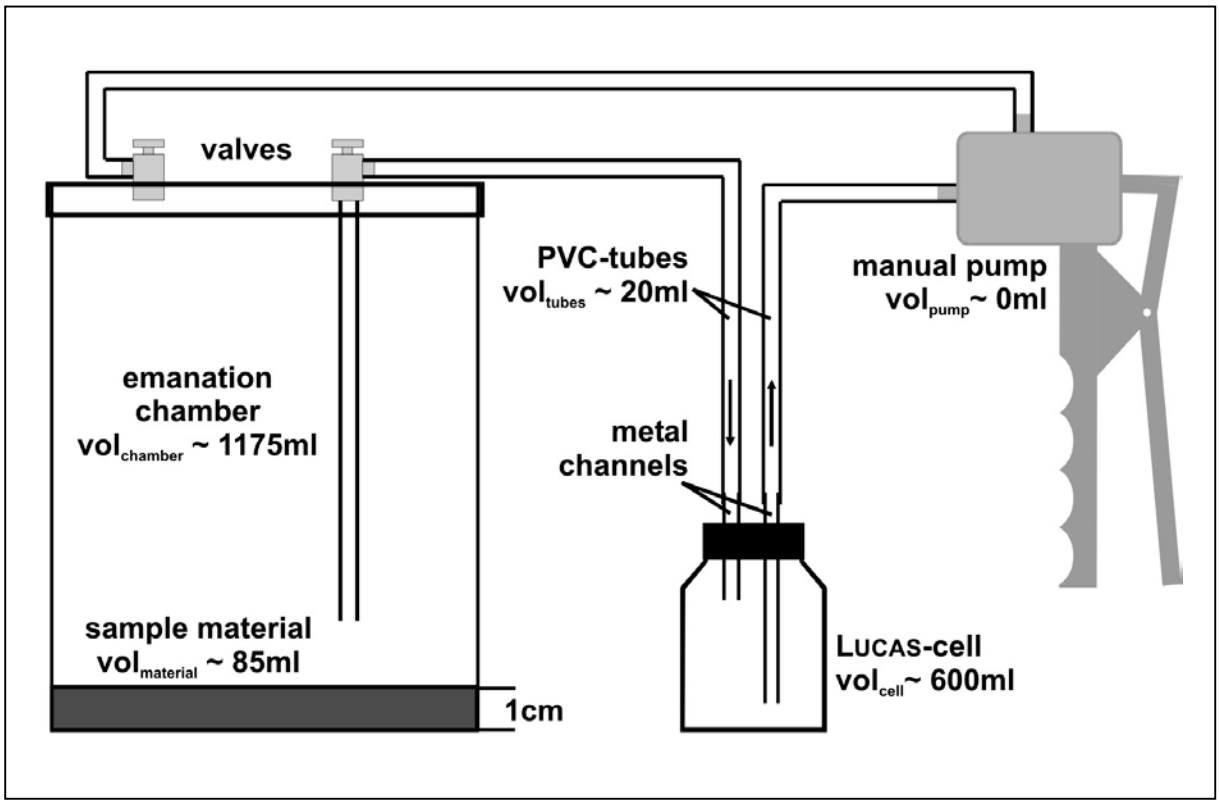

Fig 4-4: Scheme of the procedure for determining emanation coefficients (illustration based on SCHOTT, 1998).

The total radon-loss is indicated with roundabout 12%, this dimension is based on empirical measurements. The ^{222}Rn emanation rate "Er_{Rn}" is calculated by the following equation (^{222}Rn concentration c_{Rn} is calculated as described in chapter "4.4.1 600ml LUCAS-cells"):

$$Er_{Rn} = \frac{c_{Rn} \cdot f_{att} \cdot V_{air}}{m} \qquad \text{[equ. 16]}$$

Er_{Rn}: ^{222}Rn emanation rate [Bq/kg]
c_{Rn}: ^{222}Rn concentration [Bq/l]
f_{att}: factor of attenuation by Radon-free air [%]
= ($V_{chamber}$ - $V_{material}$ + $V_{LUCAS\text{-}cell}$ + V_{tubes}) / ($V_{chamber}$ - V_{sample}) [V: volume]
V_{air}: air volume in emanation chamber ($V_{chamber}$ - $V_{material}$) [l]
m: mass of dried sample material [kg]

4.4.1 600ml LUCAS-cells

In frame of determining the radon emanation coefficient, glass cells being inside alloyed with a silver endowed zinc sulphide layer (the bottom is untreated, pure glass) were used for analysing the radon concentration in air according to LUCAS (1957). Those LUCAS-cells are sized in a volume of 600ml and are designed on purpose for the scintillation counter LUK 4E made by RADON V.O.S.™ (device description is given in the appendix, chapter "A-2-d Radon measuring devices"). Before any measurement was started, the background of each LUCAS-cell has been determined. After transferring the air samples into the cells, a period of at least 3.5h was ensured to have passed by for establishing radioactive equilibrium between ^{222}Rn and its progenies. Then, the cells were put into the scintillation counter, covered and stored for 3min before the measurement was started in order to avoid any influence by light. The zinc sulphide layer is not sensitive for beta or gamma radiation, but just for alpha particles. The scintillations in the layer were generated to same portions by ^{222}Rn, ^{218}Po and ^{214}Po due to equilibrium state, registered by a photo-cathode, further transformed into electric signals and then amplified by a photomultiplier. Some interfering may be caused by ^{220}Rn of the ^{232}Th decay chain contained in air, but after 5min it can be neglected due to its short half-life of 55.6s and the storage time in the cells was fixed at 3.5h. The detection limit of this system is given by 0.015Bq/l ^{222}Rn, the radon concentration "c_{Rn}" is calculated by the following equation:

$$c_{Rn} = \frac{A_0}{V} = \frac{c_m - c_b}{2.1 \cdot t \cdot e^{-\lambda \cdot t_i}} \qquad \text{[equ. 17]}$$

c_{Rn}: ^{222}Rn-concentration [Bq/l]
A_0: activity at sample taking time [Bq]
V: volume [0.6l-LUCAS-cell]
c_m: counts measured
c_b: background counts
2.1: equipment factor [s^{-1}]
t: measuring time [s]
t_i: intermediate time between sample taking and measuring [s]
λ: disintegration factor of ^{222}Rn = $\ln 2 / t_{1/2}$ = 2.097*10^{-6}s^{-1}
$t_{1/2}$: half-life of ^{222}Rn = 328,320s

The equipment parameter is caused by the probability to detect an alpha-particle by scintillation in the zinc sulphide layer. For the 600ml LUCAS-cells, that is indicated with 70%, which means to multiply the result by 0.7. Since the scintillation is caused by alpha-particles of 3 radionuclides (^{222}Rn, ^{218}Po and ^{214}Po), the result must be divided by 3 to get the fraction of ^{222}Rn, always assuming radioactive equilibrium. Therefore, 2.1 is placed in the denominator.

4.5 Gamma dose rate

If direct access to the sample sites was enabled, the gamma dose rate was determined in-situ before the samples had been taken. For that purpose, the portable gamma scintillation counter M3 16-3 Gate Frisker made by LUDLUM™/TEXAS (the exact device description is given in the appendix, chapter "A-2-e Gamma dose rate measuring device") was put for 10s on a 1m rod and then the displayed result was taken. By measuring in 1m height, the influence of the measuring geometry was reduced compared with a measurement direct on the material, because the radius in which the gamma activity is determined by the 2" * 2" NaI-crystal is enhanced. The affecting radionuclides are ^{234}Th, ^{234}Pa, ^{226}Ra, ^{210}Pb and especially ^{214}Pb and ^{214}Bi of the ^{238}U decay series as well as ^{228}Ac, ^{228}Th and ^{208}Tl of the ^{232}Th decay series beside some of the ^{235}U decay series and ^{40}K. Therefore, the obtained dimension of gamma activity is representative for the sum of all radionuclides inclusive cosmic gamma radiation.

4.6 Uncertainty dimensions of procedures and used devices

The error dimensions of the radionuclide concentrations dissolved in the extraction fractions is a combination of statistical errors by gamma spectrometric measurements, weighting the sample material and systematic errors as well. The latter can be caused by wrong sample taking, not complete homogeneous mixing of sieved/crushed sample material and precipitation or fractioning of particles in frame of solidifying the extraction liquids in the 250ml MARINELLI-beakers.

4.6.1 Uncertainty of initial activity concentrations

The statistical error consists of the error given by the weight machine (0.0025%) and the uncertainty calculated by the gamma-spectrometry software (InterWinner 5.0 made by ORTEC™). According to ORTEC (2002), that calculation is undertaken as follows, the definitions of $counts_{gross}$, background and $width_{ROI}$ are given in the appendix, chapter "A-2-a Gamma-spectrometry":

$$uncertainty = \frac{\sqrt{counts_{gross} + background \cdot \frac{width_{ROI}}{6}}}{counts_{netto}} \cdot 100 \qquad \text{[equ. 18]}$$

For determining the average error dimension calculated by the software, those relative uncertainties were taken from each radionuclide, summed up and then the total arithmetic average error was calculated. The minimum was given by 5% and the maximum by 48%, the average uncertainty amounts to 10.4%. In comparison with that dimension, the error by the weight machine can be neglected.

4.6.2 Uncertainty of activity concentrations in extracted fractions

The uncertainty of an extracted fraction is a combination of systematic and statistical errors in frame of the extraction procedure, the analysis of the liquid's radionuclide concentrations and the determination of the initial activity concentration as well.

The statistical errors for the extraction procedures are due to the uncertainty of the weight machine (0.05%) and to the adding of the chemical reagents' volume. The latter is given by 1ml, which means for the extraction volumes of 200ml 0.5% and for the last BCR step of 250ml 0.4%. Systematic errors can be caused by deviating times of shaking the extractions, contaminated glasses or vessels or temperature changes during extraction.

Systematic errors in frame of gamma-spectrometry measurements can be caused by impurities inside the MARINELLI-beakers. The relative uncertainties of the extraction liquids' radionuclide concentrations should not exceed 20%. The uncertainties of the initial activity concentration are described in chapter "4.6.1 Uncertainty of initial activity concentrations".

4.6.3 Total uncertainty of extracted fractions

The relative total uncertainty σ of an extraction fraction can be calculated according to the uncertainty propagation code by using the parameters calculated above:

$$\sigma = \sqrt{2 \cdot 0.104^2 + 0.2^2 + 0.0005^2 + 0.004^2} = 0.248 = 24.8\%$$

That means in summary, per extraction fraction a maximum total uncertainty of 25% must be assumed.

4.6.4 Total uncertainty of radon emanation

The relative statistical uncertainty τ of the radon emanation was calculated according to equation 19:

$$\tau = \sqrt{\frac{\frac{c_m}{t} + \frac{c_b}{t}}{(c_m - c_b)^2} + \sum_1^i \left(\frac{s(i)}{i}\right)^2} \qquad \text{[equ. 19]}$$

c_m: number of counts measured [s^{-1}]
c_b: number of background counts [s^{-1}]
t: measuring time [s]
s: measurand error
i: measurand

measurand error:	0.07 standard deviation of 600ml LUCAS-cell's efficiency
	0.002l standard deviation of 600ml LUCAS-cell's air volume
measurands:	efficiency of 600ml LUCAS-cell (70%)
	air volume of LUCAS-cell (600ml)

The left term of the root is due to the uncertainty of counting impulses by the scintillation counter, the right is caused by the calculation of the ^{222}Rn concentration. The measurands and their errors are independent from each other and therefore, the uncertainty propagation is based on GAUSS. The product of relative statistical uncertainty and ^{222}Rn concentration results in the absolute statistical uncertainty (WIEGAND, 1999).

5 Results

The results are separated into four chapters dealing with the initial radionuclide contents, the dissolved radionuclide fractions by extraction procedures, the radon emanation rates and finally the gamma dose rates are presented for those investigation sites where access was enabled.

5.1 Initial radionuclide content

In order to evaluate the initial activity concentrations of the radionuclides, the samples' grain size fraction <2mm was measured by gamma-spectrometer (except the powdered samples W-FD-1 and P-FZM-2 from refractory production), because the solid calibration standard is also made of a concrete matrix <2mm. By taking the same grain sizes, the influence of that parameter is reduced as low as possible. The given uncertainties quote to 2σ confidence.

5.1.1 Phosphate industry

Five samples from the fertiliser production were delivered covering the whole production process. The two raw materials are quite different in the dimensions of their radionuclide concentrations due to their different deposit origin, but as to be expected for undisturbed natural materials, both show respective radioactive equilibriums (fig. 5-1). R-PO-1 is a sedimentary phosphate bearing ore from Morocco showing the radionuclides of the ^{238}U decay series in

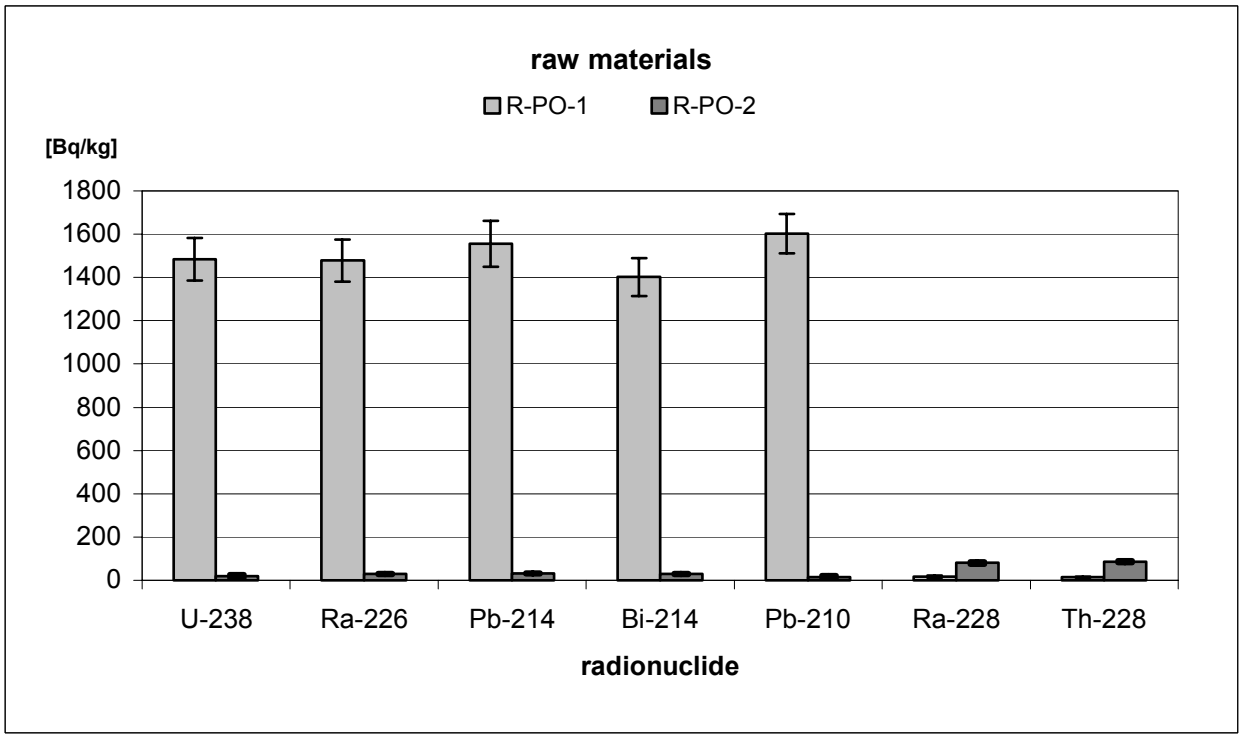

Fig. 5-1: Initial activity concentrations of the phosphate ores R-PO-1 and R-PO-2.

concentrations of 1500Bq/kg whereas the ^{232}Th decay series' radionuclides are present in concentrations lower than 20Bq/kg. R-PO-2 comes from the Russian Kola peninsula, which is an igneous phosphate ore deposit. The ^{238}U radionuclides concentrations range around 25Bq/kg, those of $^{232}Th_{nat}$ are of 50Bq/kg. Both materials' activity concentrations are in well accordance with the dimensions given in literature (see chapter "3.1.2 Produced TENORM"). The waste material phosphogypsum is not to be classified as TENORM, because its radionuclide content is

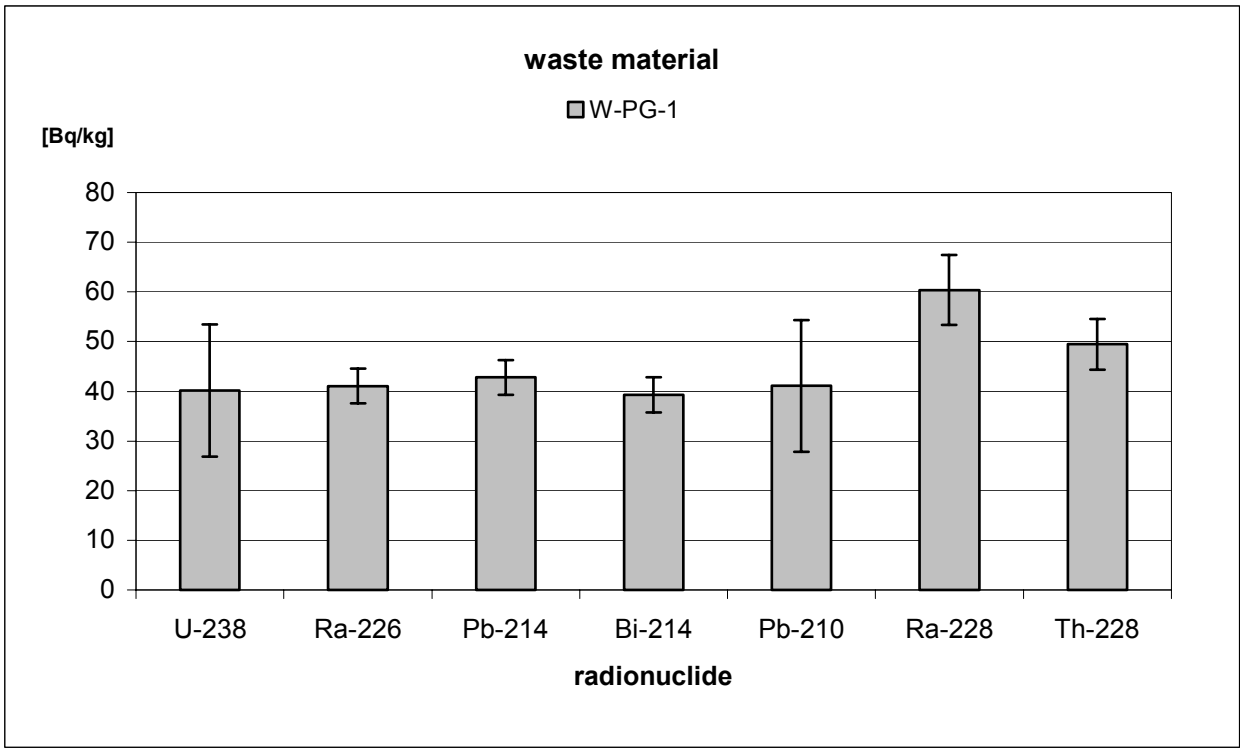

Fig. 5-2: Initial activity concentrations of the phosphogypsum W-PG-1.

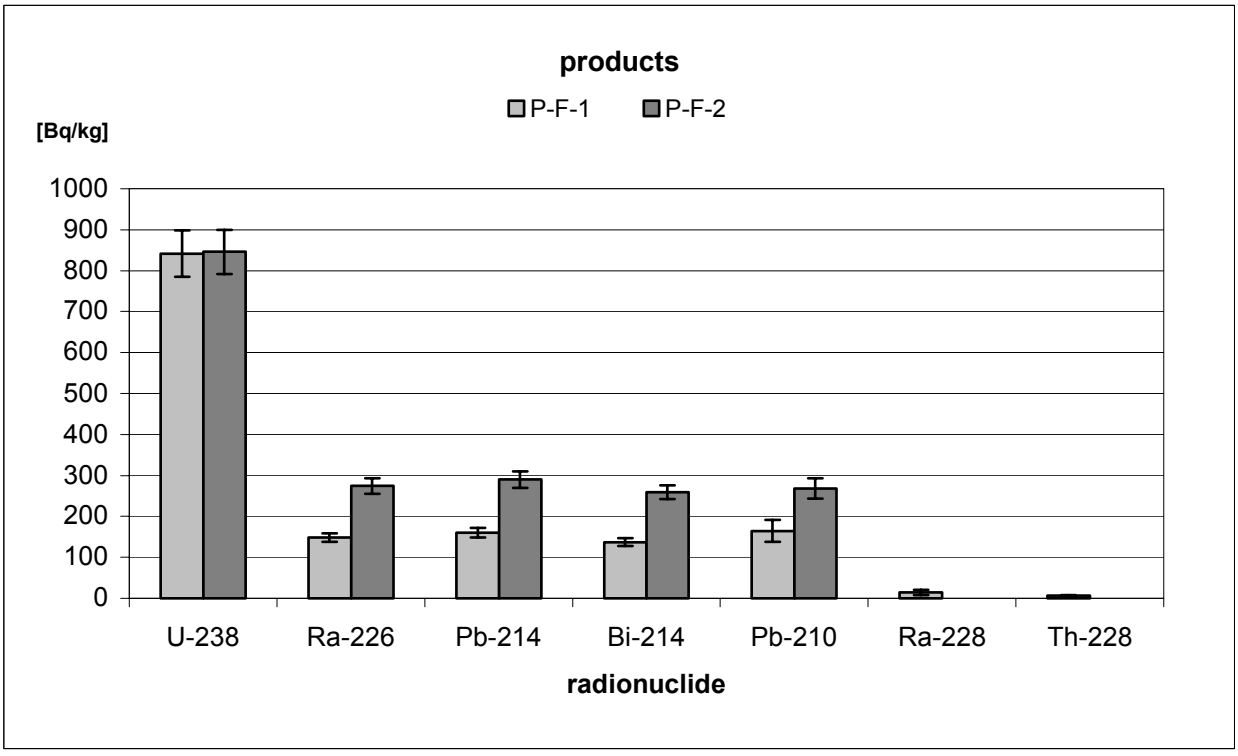

Fig. 5-3: Initial activity concentrations of the fertilisers P-F-1 and P-F-2.

constantly below 200Bq/kg, showing the radionuclides in respective equilibrium (fig. 5-2). In contrast, both the fertiliser products, NPK- (P-F-1) and PK-type (P-F-2), are characterised by strong enhanced uranium concentrations, which are almost identically higher than 800Bq/kg (fig. 5-3). ^{226}Ra, ^{214}Pb, ^{214}Bi and ^{210}Pb vary between 150 and 250Bq/kg, ^{228}Ra and ^{228}Th are not mentionable present. For the production process a mixing of both the phosphate ores can be assumed, because there is almost no difference in the radionuclide concentrations for both fertiliser types. That means the uranium transfer is set from the raw material towards the product, waste material is not affected. The very most of the initial radium concentration is removed from the production process by discharging waste water as shown by high concentrations (up to 14,000Bq/kg for ^{226}Ra) in sediments along sewers or rivers (POFFIJN & DE CLERK, 2004).

5.1.2 Aluminium industry

In frame of the aluminium production the raw material bauxite and the produced waste material red sludge may be affected by enhanced concentrations of natural radionuclides. Two bauxite samples were investigated, R-AO-1 imported from Boke-zone, Guinea-Bissau, R-AO-2 from Trombeta-zone, Brazil, and the different sources are also visible in the different dimensions of radionuclide content (fig 5-4). Sample R-AO-1 shows relatively low activity concentrations for both decay series' of roundabout 200 Bq/kg, whereas R-AO-2 is characterised by strong elevated concentrations for the uranium decay series, ^{232}Th progenies stand back. ^{238}U is of 800Bq/kg and ^{226}Ra increases up to more than 2000Bq/kg, the highest value is given by ^{210}Pb with almost 4000Bq/kg. It is typical for both samples being not radioactively equilibrated that the highest activity concentrations are represented by ^{210}Pb. The measured radionuclide concentrations are in

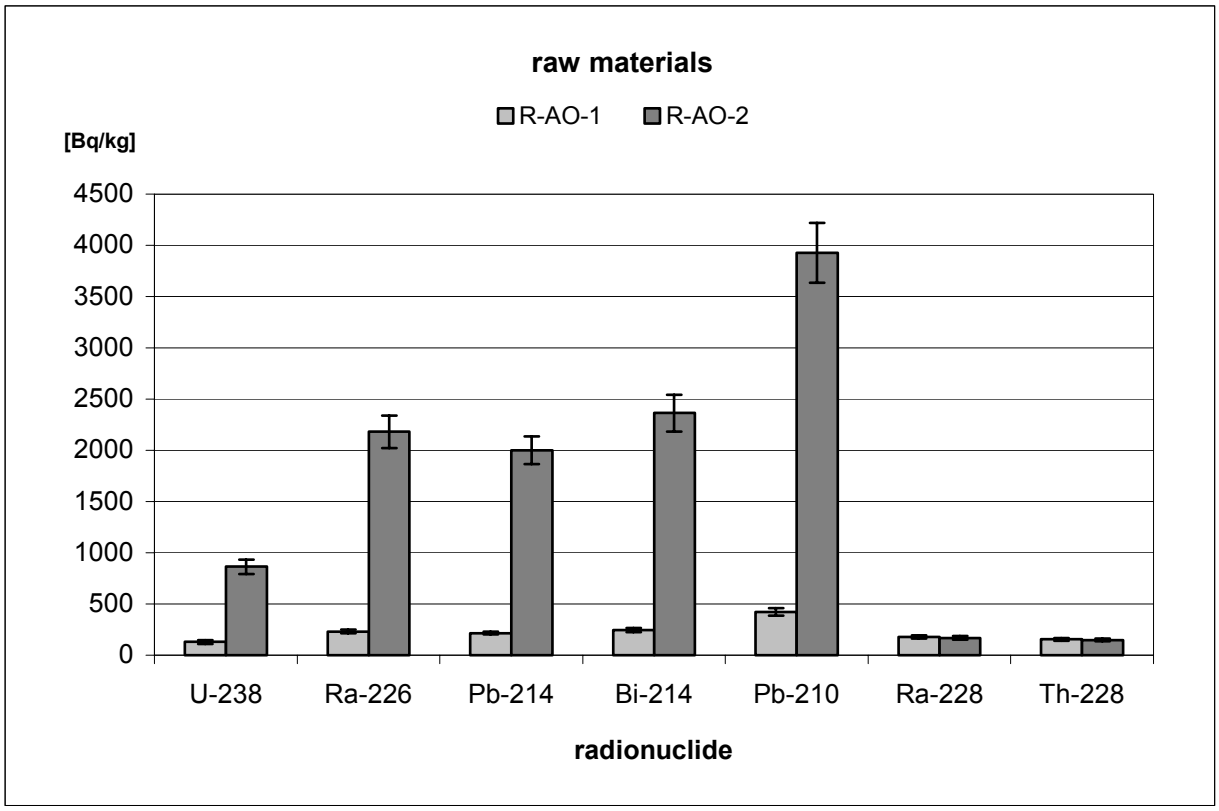

Fig. 5-4: Initial activity concentrations of the aluminium ores R-AO-1 and R-AO-2.

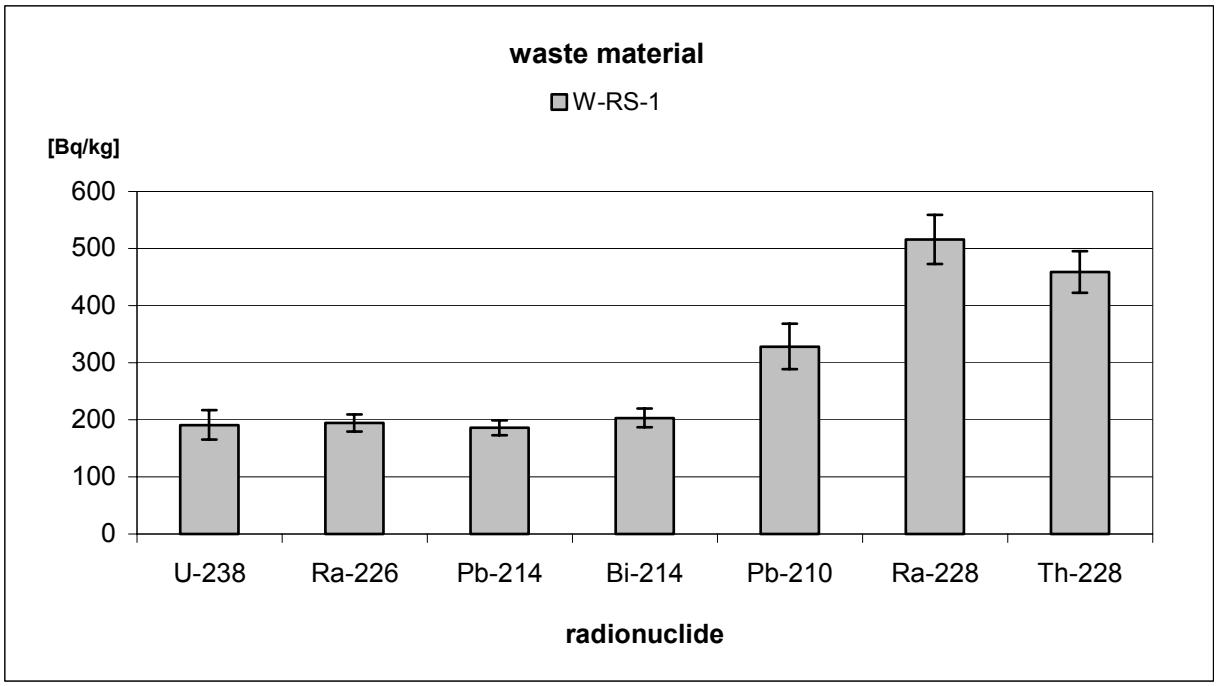

Fig. 5-5: Initial activity concentrations of the red sludge W-RS-1.

agreement with those mentioned by RADULESCU & POPESCU (2002a). The waste red sludge shows similar radionuclide ratios for the ^{238}U decay series, but in one magnitude lower dimensions, the highest value is given by ^{210}Pb with more than 300Bq/kg (fig. 5-5). As it is reported, the final product aluminium does not contain any mentionable radionuclide concentration (PENFOLD et al, 1999), therefore, the reduced radionuclide content in the waste is may due to delution during processing or leaching processes on the sludge's surface. The radionuclides of the ^{232}Th decay series are present in the waste at roundabout 500Bq/kg. In comparison with the raw materials, this is an enhancement factor of 3 due to manufacturing.

5.1.3 Refractory industry

Some refractory materials and resulting waste materials are of radiological interest due to high radionuclide contents in the additive raw material zircon sand. The zircon sand sample R-ZS-1 shows for all radionuclides of the ^{238}U decay series equilibrated activity concentrations ranging between 2500 and 3000Bq/kg, ^{228}Ra and ^{228}Th are present of about 700Bq/kg (fig. 5-6). These dimensions are in agreement with those given in literature (see chapter "3.2.2. Produced TENORM"). The dust from heating the raw materials is collected by filters and the filter dust sample W-FD-1 shows absolutely strong enhanced ^{210}Pb activity concentrations of more than 160,000Bq/kg, all other radionuclides are of roughly 200Bq/kg (fig. 5-7). This corresponds to a lead enhancement factor of 65 caused by its volatilisation in frame of heating the raw matrials, which consequently results in a depletion in the final product fused zirconia mullite (FZM). Both samples P-FZM-1 and P-FZM-2 are therefore characterised by lower ^{210}Pb concentrations than contained in the raw material, the dimensions are of 1000Bq/kg in both cases (fig. 5-8). Although P-FZM-1 is of a grain size <2mm and shows activity concentrations for all other relevant radionuclides at almost half of the powdered sample P-FZM-2 <0.1mm, both have the same lead

concentrations. That leads to the conclusion that in this case the influence by different grain sizes is not of strong importance. The activity concentrations are of 4000Bq/kg for the ^{238}U and

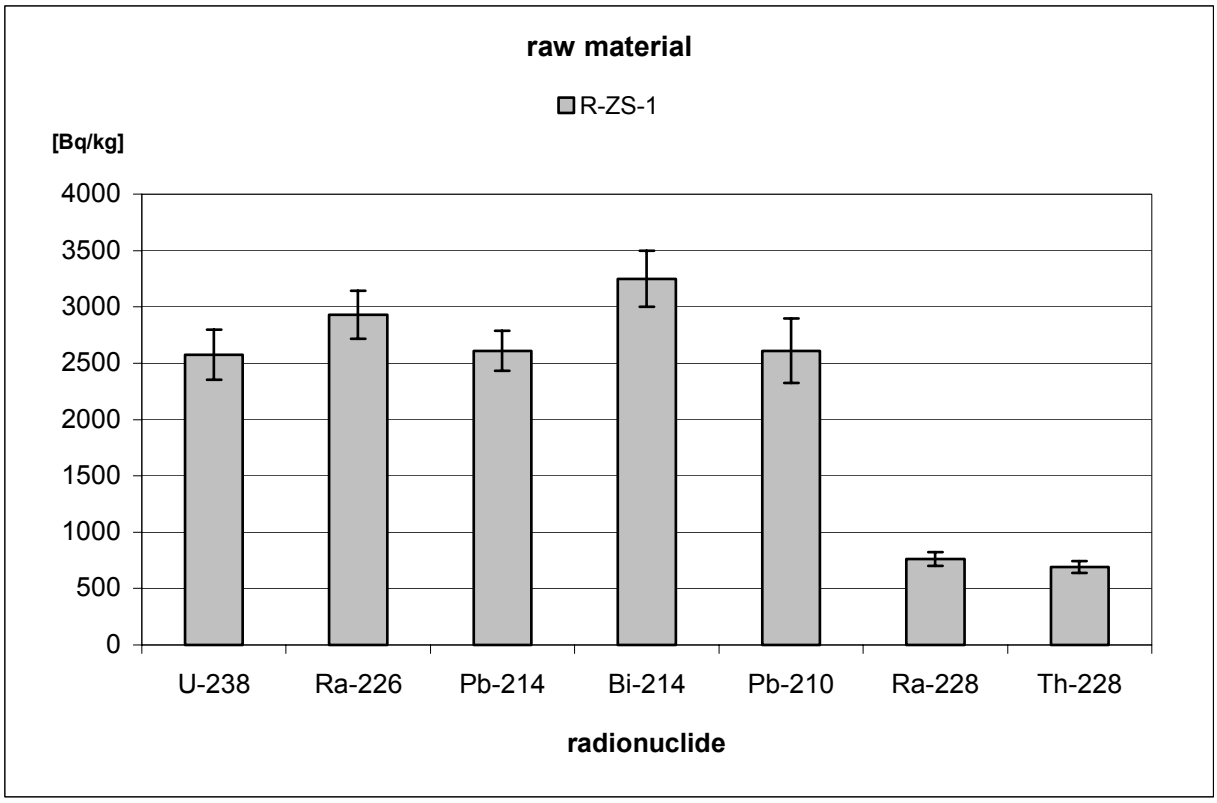

Fig. 5-6: Initial activity concentrations of the zircon sand R-ZS-1.

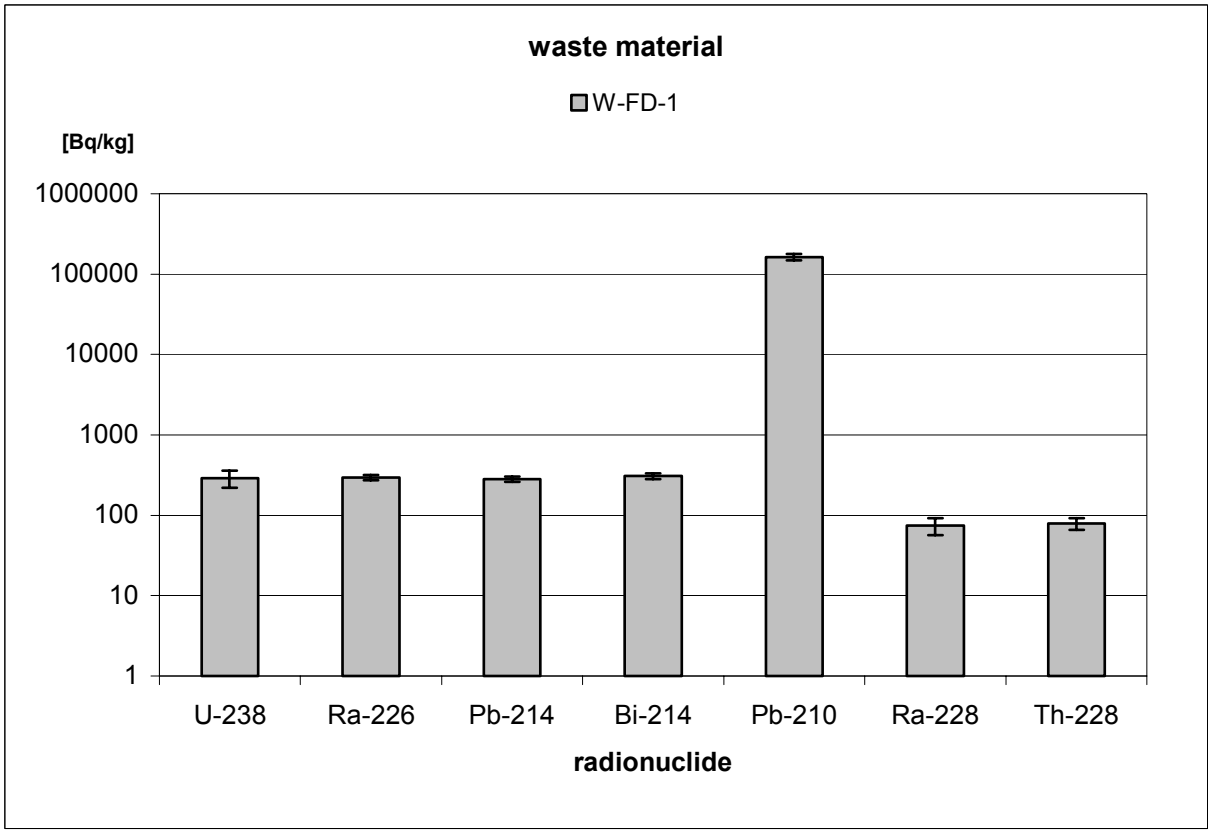

Fig. 5-7: Initial activity concentrations of the filter dust W-FD-1.

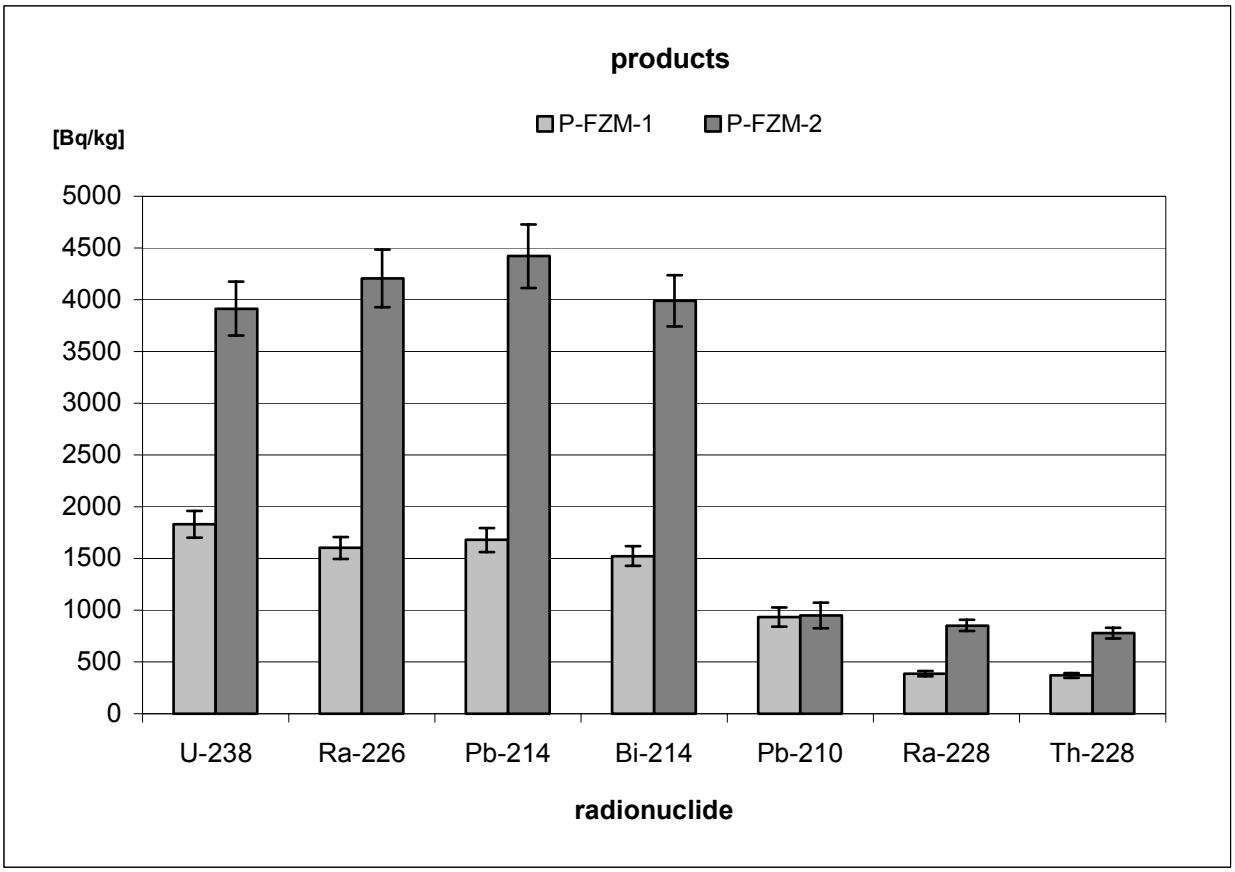

Fig. 5-8: Initial activity concentrations of the fused zirconia mullites P-FZM-1 and P-FZM-2.

800Bq/kg for the ^{232}Th progenies in P-FZM-2, in P-FZM-1 of a half, and in both cases they are in respective radioactive equilibrium.

5.1.4 Crude oil exploitation

The crude oil exploitation produces two typical types of material, which usually contain really high concentrations of natural radionuclides: sludge and scales, each is represented by two samples. The sludge samples W-SL-1 and W-SL-2 show some ten thousands Bq/kg for the radionuclides of the ^{238}U decay series in almost equilibrated state (fig. 5-9), W-SL-1 in the range around 20,000Bq/kg with slightly higher ^{210}Pb concentrations, those of W-SL-2 in dimensions of 45,000Bq/kg. In both samples the ^{232}Th progenies are of a quarter compared with ^{238}U. The scales W-SC-1 and W-SC-2 are characterised by especially high ^{210}Pb concentrations of 45,000Bq/kg, ^{226}Ra and progenies stand back by lower than 10,000Bq/kg in W-SC-2, in W-SC-1 the half of that (fig. 5-10). ^{228}Ra and ^{228}Th are rather low. In all four samples no uranium activity concentrations were detected. All these measured radionuclide concentrations are representative for the milieu the materials are formed in frame of crude oil extraction. The sludge samples are solids from suspensions remaining in vessels, whereas the scales are due to precipitation processes encrusting pipelines and other installations, the high lead concentrations as a consequence of the radon decay in those gaseous dense areas.

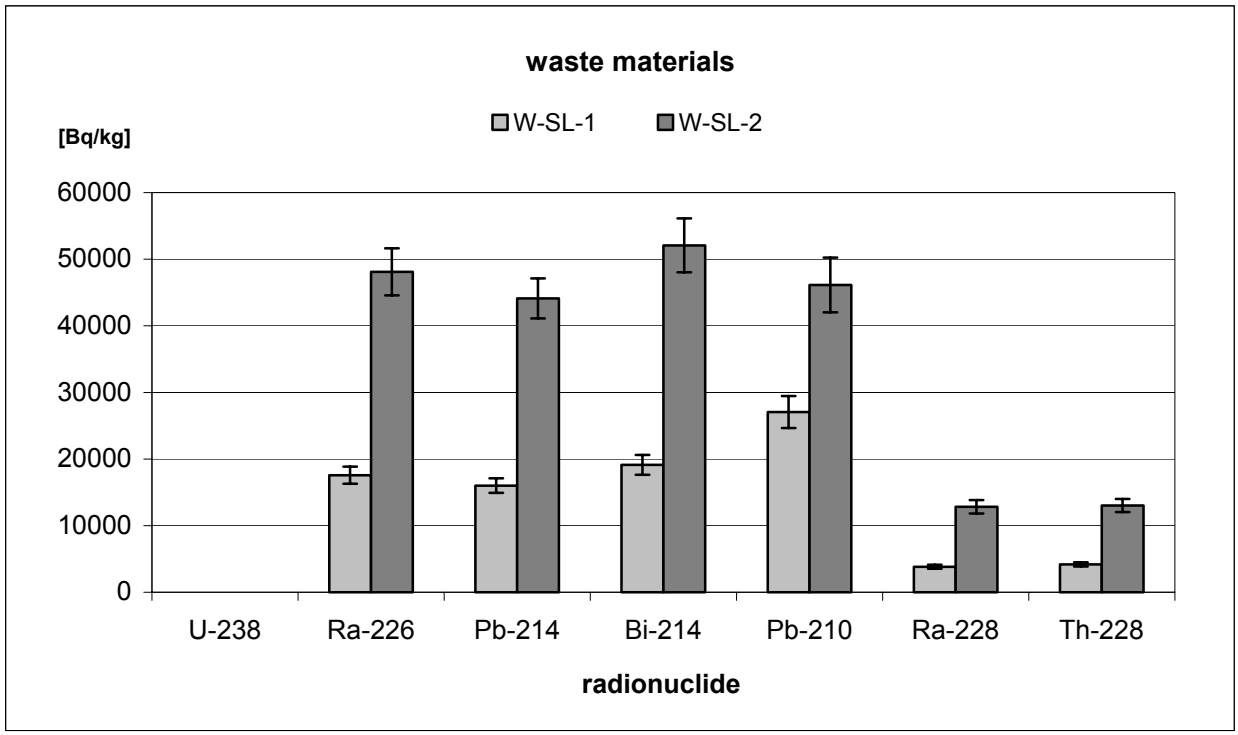

Fig. 5-9: Initial activity concentrations of the sludge samples W-SL-1 and W-SL-2.

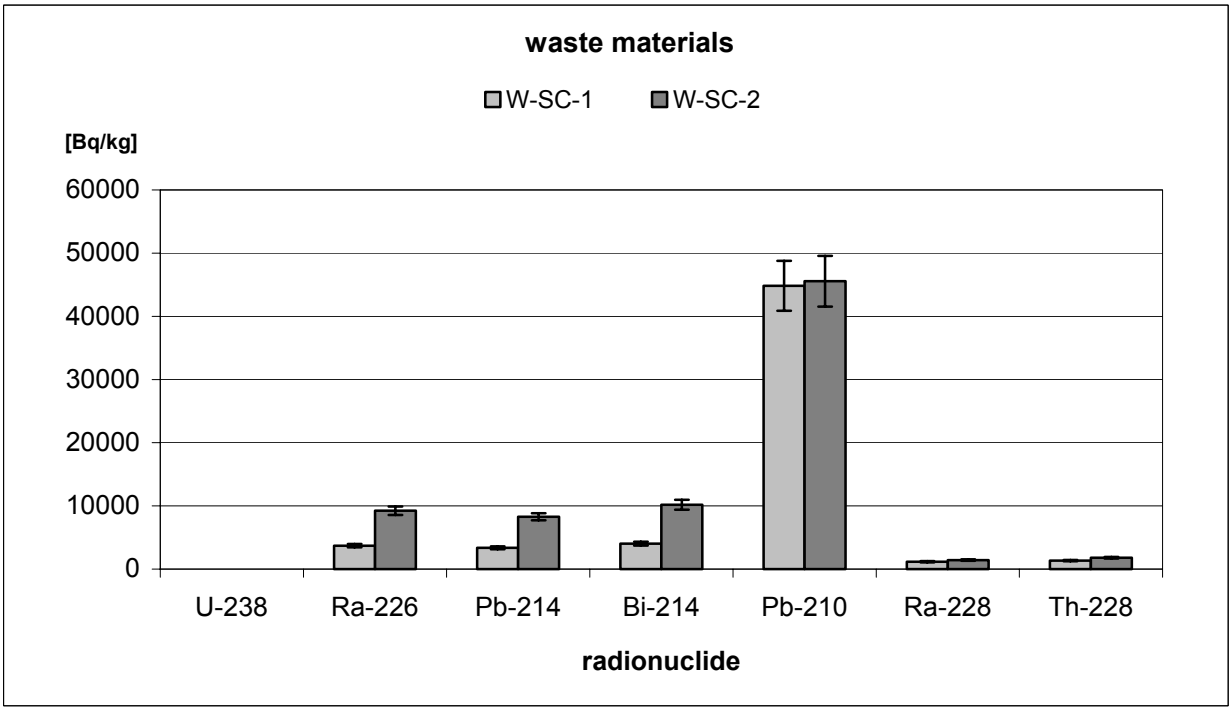

Fig. 5-10: Initial activity concentrations of the scales W-SC-1 and W-SC-2.

5.1.5 Hard coal extraction

Hard coal extraction is usually connected with pumping groundwater to the surface and discharging that as pit waters into sewers or tributaries. There, those waters can lead to enhanced radionuclide concentrations in sediments along the rivers, if they are contaminated and are

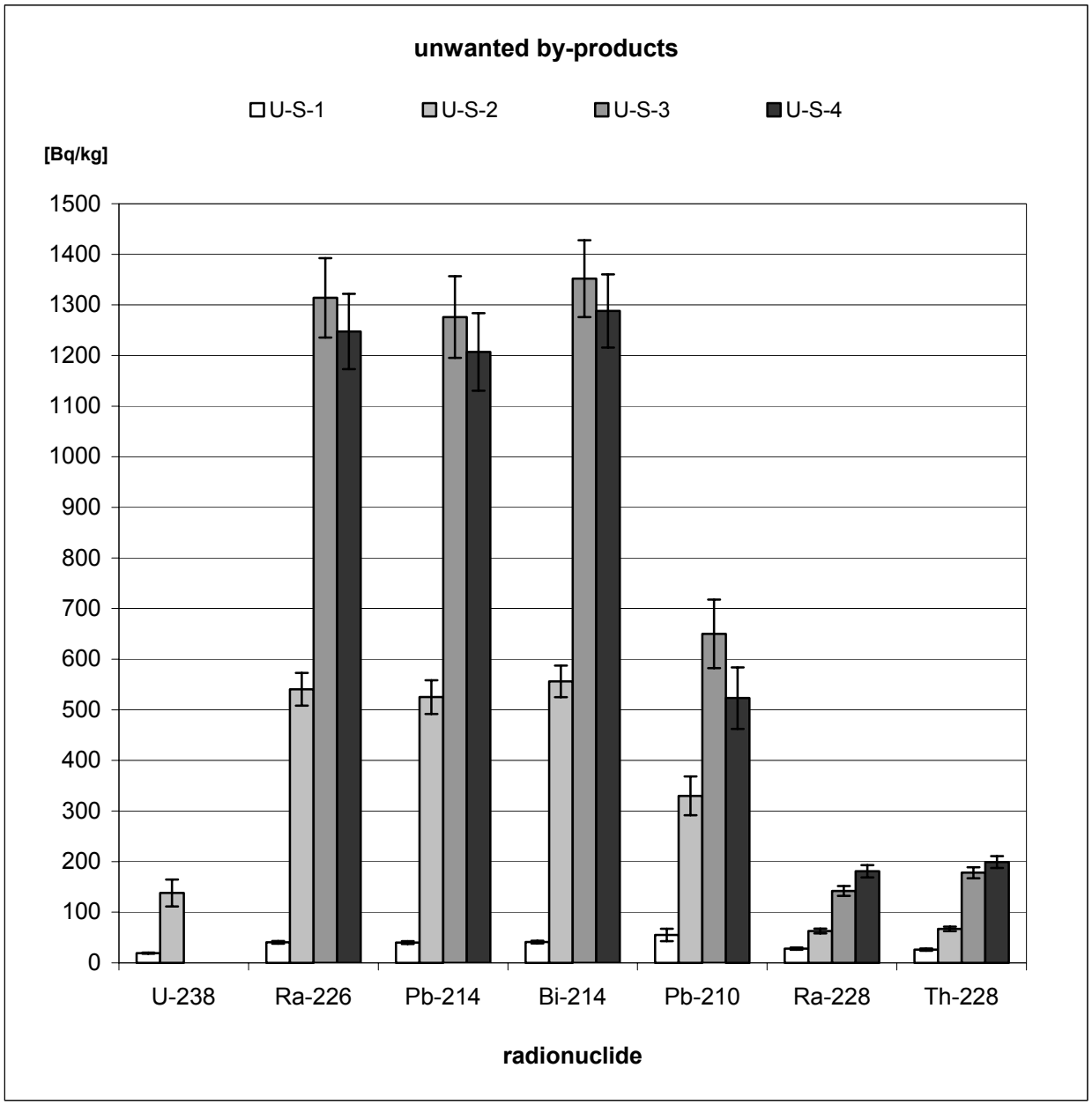

Fig. 5-11: Initial activity concentrations of the sediment samples U-S-1, U-S-2, U-S-3 and U-S-4.

exposed to oxidising milieus and barium is present (CHALUPNIK et al., 2001, SCHMIDT & WIEGAND, 2003). Four samples from those sediments were taken at different positions of a riverside. U-S-1 is characterised by activity concentrations being constantly lower than 50Bq/kg for all radionuclides (fig. 5-11) and was taken as background sample without any influence by river water. U-S-2 represents a soil being irregularly affected by flood events and contains ^{226}Ra concentrations of more than 500Bq/kg, ^{210}Pb around 350Bq/kg, but uranium and ^{232}Th progenies are of background dimensions. U-S-3 and U-S-4 were taken directly on the waterline, U-S-3 at slip-off slope and U-S-4 at undercut slope. Both show well corresponding radionuclide concentrations: uranium is not present, ^{226}Ra ranges around 1200 and 1300Bq/kg, ^{210}Pb is of 500-600Bq/kg and ^{228}Ra and ^{228}Th are of 150Bq/kg. That leads to the conclusion that the position of either slip-off or undercut slope is not of importance for the dimension of ^{226}Ra activity concentration in case of contamination by discharged pit waters. The lead concentrations in U-S-2, U-S-3 and U-S-4 are due to growing again from its decaying parent nuclide ^{226}Ra.

5.1.6 Thorium compounds industry

As representatives of the thorium compounds using industry residue samples were provided from two different production processes: one soil sample is contaminated by remnants from the former performed FISCHER-TROPSCH-synthesis using thorium-cobalt catalysts (U-SO-1) and three soil samples are affected by the dust created during the destruction of a former gas mantle factory by an air-raid (U-SO-2, U-SO-3 and U-SO-4). U-SO-1 is characterised by constantly high activity concentrations of all relevant radionuclides (fig. 5-12), especially of the ^{232}Th progenies ^{228}Ra (500,000Bq/kg) and ^{228}Th (420,000Bq/kg), but also ^{238}U (15,000Bq/kg). The elevated concentrations of uranium seem to be due to the additional production of uranium at the respective site (GELLERMANN et al., 2003). U-SO-2 and U-SO-3 contain ^{228}Ra and ^{228}Th in equilibrated concentrations of almost 10,000Bq/kg each, the uranium decay series is constantly present in dimensions of roughly 1000Bq/kg. All the activity concentrations of U-SO-4 deviate from those mentioned before not exceeding the 100Bq/kg limit and is therefore not a

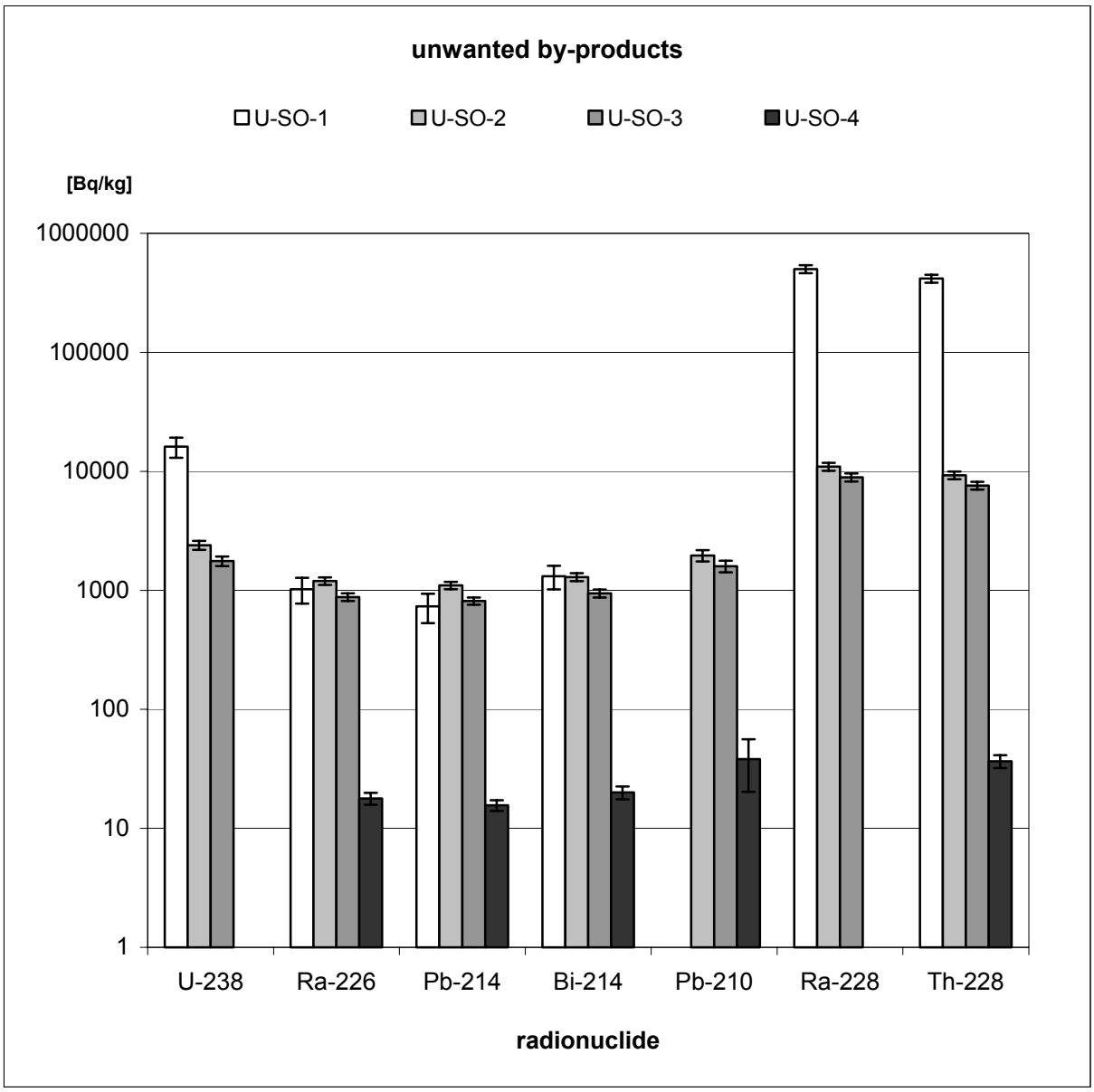

Fig. 5-12: Initial activity concentrations of the soil samples U-SO-1, U-SO-2, U-SO-3 and U-SO-4.

TENORM. This might be explained by the inhomogenous distribution of the radionuclide bearing dust among the gas mantle factory's area, which is in accordance with the annual report by MLUV (2002), so that sample's radionuclide content is just of natural background.

5.1.7 Uranium industry

From the uranium processing industry the by far most samples were available, but delivered from two different sites. The uranium ore bearing hard rocks and the tailings come from the Slovenian Zirovski vrh mine close to Gorenja Vas, the unwanted by-products from stockpiles and tributary sediments are derived from the former mining area of Pribram, Czech Republic. The raw materials R-UO-1 and R-UO-2 show differing activity concentrations for the ^{238}U decay series, that of ^{232}Th is not present (fig. 5-13). But as to be expected for those natural hard rocks, both samples show equilibrated states for the U_{nat} radionuclides: R-UO-1 around 100,000Bq/kg and R-UO-2 much higher of almost 900,000Bq/kg. This difference is due to the inhomogenous dispersion of uranium minerals within the rocks. The unwanted dead rocks or slags heaped up in stockpiles show varying activity concentrations, too, and also in respective radioactive equilibrium each (fig. 5-14). The slag samples U-ST-1 and U-ST-2 contain the relevant radionuclides in maximum concentrations of 200Bq/kg including ^{228}Ra and ^{228}Th and therefore, the TENORM definition is not fulfilled. The light coloured pegmatite sample U-ST-3 is characterised by uranium and progenies contents of roundabout 1000Bq/kg, this is typical for lateral and therefore hardly interspersed ore bearing rocks. U-ST-4 is a red coloured sandstone breccia of tectonic origin, whose rock surface is partly coated with black pitchblende spheroids. That causes the high activity concentrations of more than 100,000Bq/kg for almost all radionuclides of the uranium decay series. A detailed geological rock description of all six hard rock samples is given in the appendix, chapter "A-1 Material descriptions". The sediment samples represent two

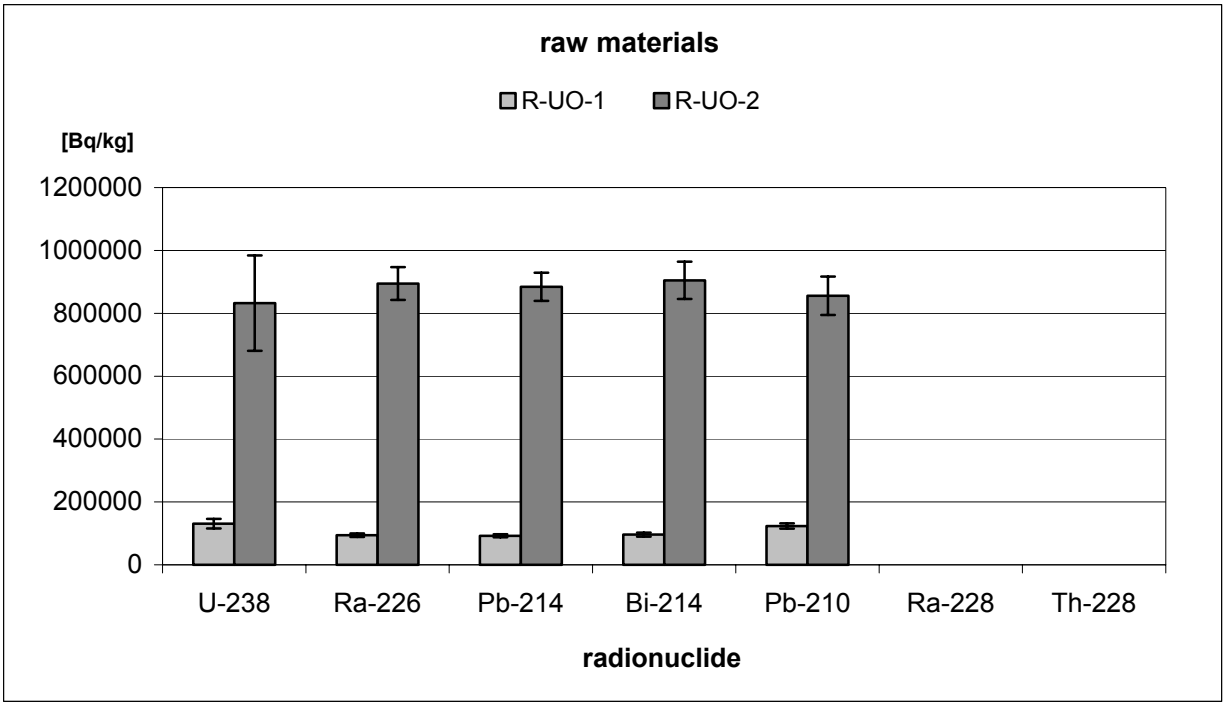

Fig. 5-13: Initial activity concentrations of the uranium ores R-UO-1 and R-UO-2.

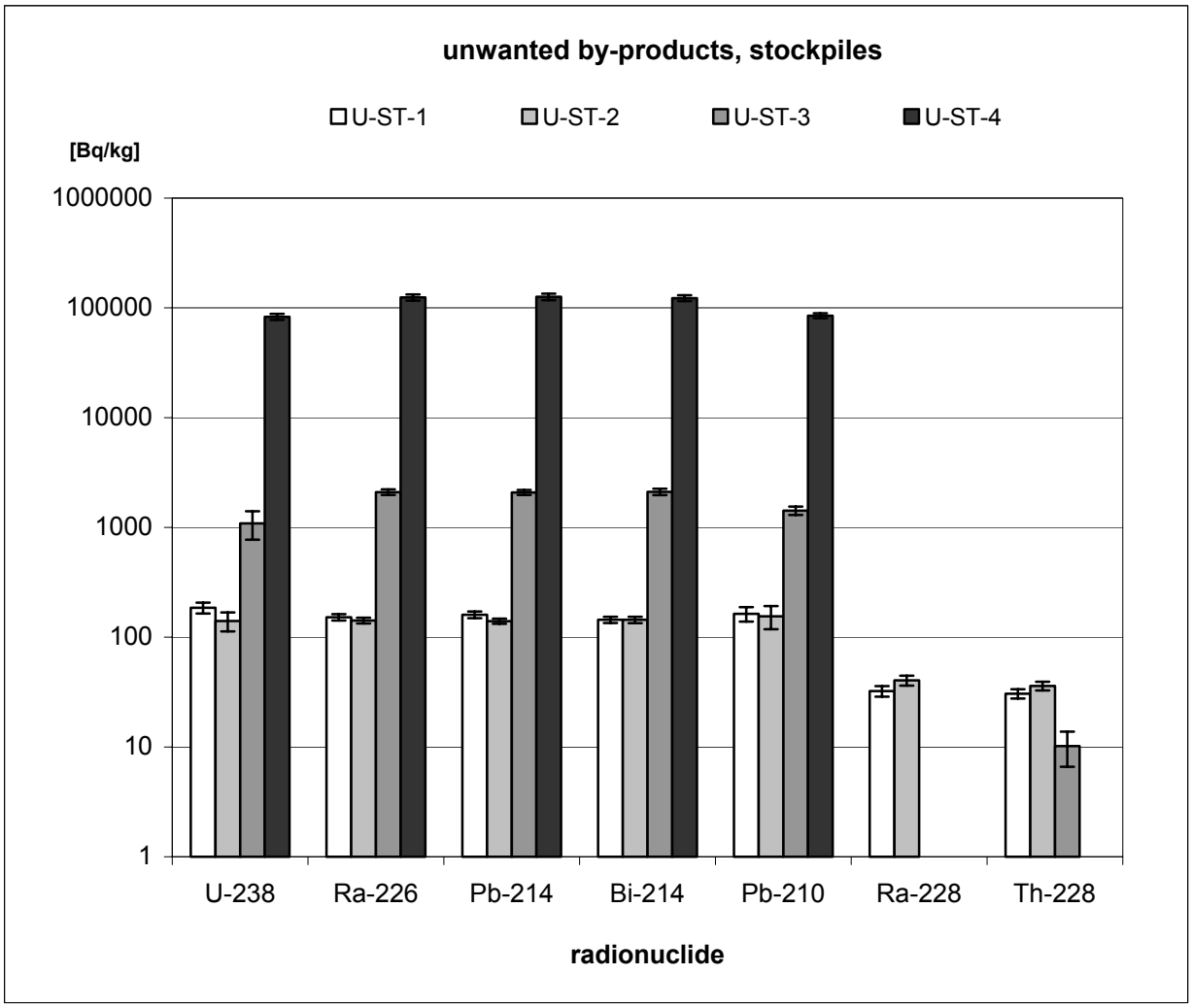

Fig. 5-14: Initial activity concentrations of the stockpile samples U-ST-1, U-ST-2, U-ST-3 and U-ST-4.

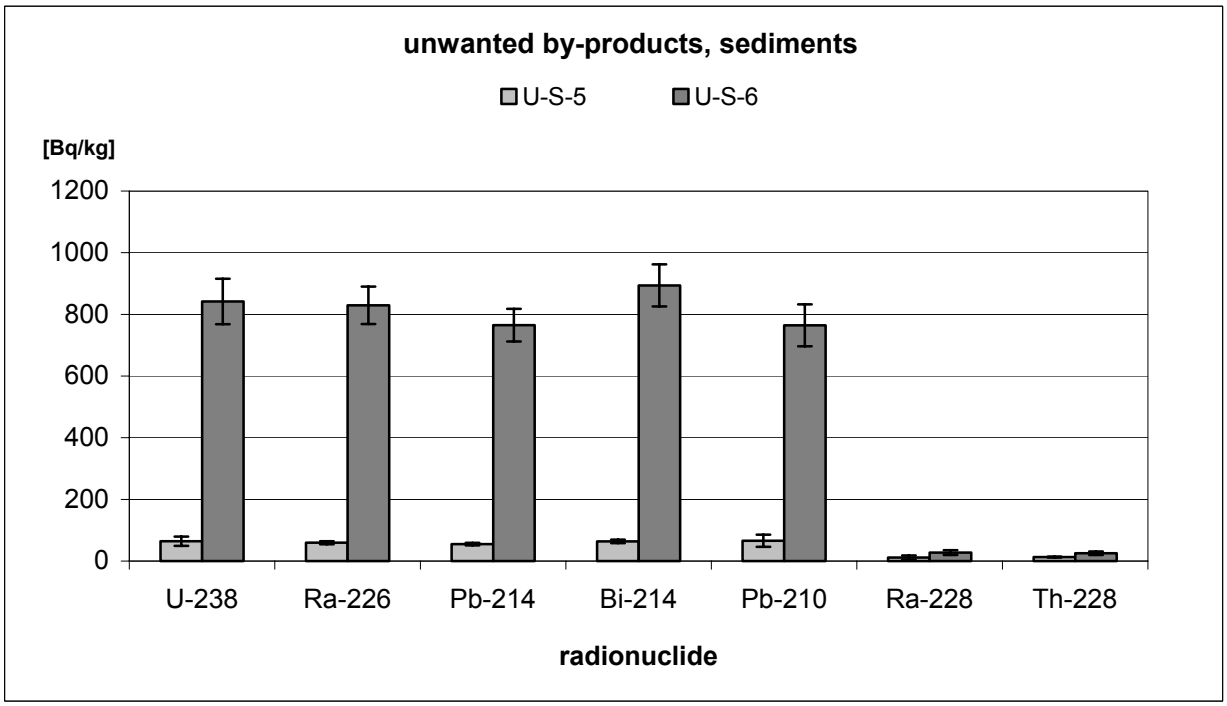

Fig. 5-15: Initial activity concentrations of the sediment samples U-S-5 and U-S-6.

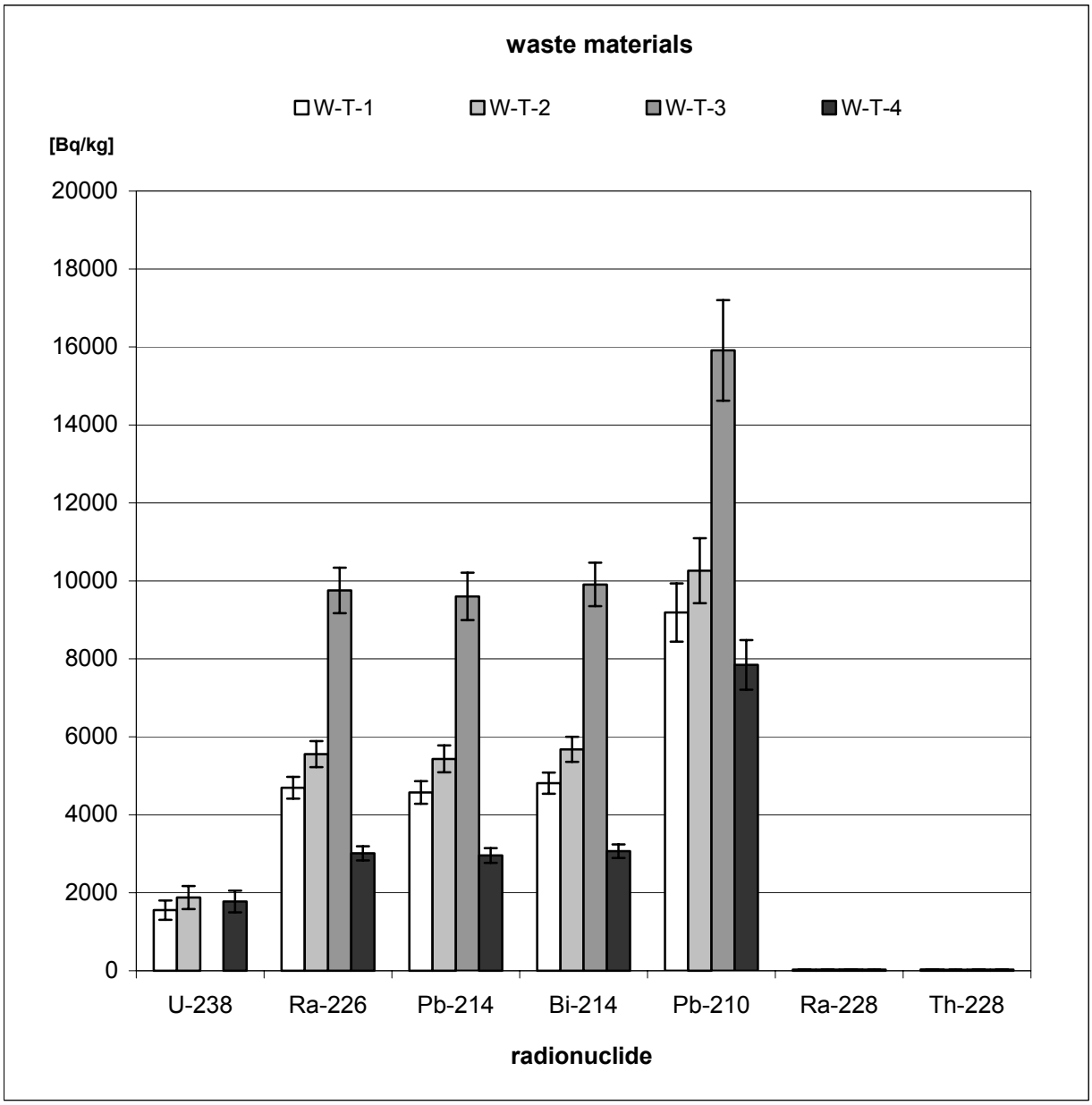

Fig. 5-16: Initial activity concentrations of the tailings W-T-1, W-T-2, W-T-3 and W-T-4.

different milieus: U-S-5 was taken before any influence by heaped up materials must be taken into consideration and therefore as a background sample, whereas U-S-6 was taken downstream of a tailing pond's tributary of natural state. All the radionuclide concentrations in U-S-5 do not exceed the 100Bq/kg limit, but U-S-6 shows enhanced activity concentrations in equilibrated state for all the relevant radionuclides of the uranium decay series ranging around 800Bq/kg, ^{232}Th progenies are no objects (fig. 5-15). This enhancement seems to be due to some leaching processes within the tailings a few hundred meters upstream and a succeeding precipitation along the sewer. Within the Slovenian tailing pond of the Zirovski vrh mine, four samples were taken at different points, the material having been of homogenous composition as also described by KRIZMAN et al. (1995). As shown in fig. 5-16, they vary in the dimensions of their radionuclide concentrations, which are not equilibrated, but the tendency is the same for all: rather low uranium concentrations due to the leaching from the ores (W-T-3 does not contain any uranium activity), ^{226}Ra is higher than 2500Bq/kg up to almost 10,000Bq/kg and the maximum activity

Table 5-1: Correlation coefficients for the uranium decay series' radionuclides in the tailing samples.

radionuclide	W-T-1	W-T-2	W-T-3	W-T-4
^{238}U	0.17	0.18	- / -	0.22
^{226}Ra	0.51	0.54	0.61	0.38
^{214}Pb	0.49	0.53	0.6	0.38
^{214}Bi	0.52	0.55	0.62	0.39
^{210}Pb	1	1	1	1

concentrations are caused by ^{210}Pb, which range from 8000Bq/kg up to 16,000Bq/kg. The resulting correlation coefficients for those radionuclide contents in each sample are given in table 5-1, taking the respective ^{210}Pb concentration as the basis. KRIZMAN et al. (1995) observed the same concentration dimensions and also such strong unbalanced radionuclide ratios in the Zirovski vrh mine's tailings, in average described for ^{230}Th (4000Bq/kg) and ^{226}Ra (8000Bq/kg). They explained this phenomenon by some co-leaching of uranium's next progenies in frame of its extraction process, which was also observed in Canada by MOFFETT (1977) almost two decades ago. That model corresponds very well with the radionuclide ratios presented in table 5-1, but a further leaching of ^{226}Ra after storage, especially on the surface, should be taken into account, too.

5.2 Radionuclide fractions dissolved by extraction procedures

The chemical type of bounding of the natural radionuclides and their mobilisation potential were investigated by the application of three different extraction procedures according to European and German standards. The dissolved radionuclide fractions from the sequential BCR extraction procedure are given as a portion of 100%, because all the three fractions were obtained step by step from the same amount of starting sample material. If an undissolved amount of the initial radionuclide content remained, it is shown as residual in the diagram. When the sum of all three fractions for one radionuclide exceeded the total of 100%, they were recalculated according to their portion in order to avoid dissolved radionuclide amounts of more than 100%. In case of both the German single step extraction procedures, the dissolved radionuclide amounts are simply presented as a portion of 100% due to their single step character. Usually, the material's grain size <2mm was taken for the extraction procedures. But if the solid material's volume was large enough, the sample was separated into the fractions <2mm and <0.1mm for investigating the influence of the grain size towards the radionuclide's availability.

In the appendix, chapters "A-3 Radionuclide portions extracted by BCR procedure" and "A-4 Radionuclide portions extracted by DIN 19730 and DIN 38414/S4 procedures", all the absolute radionuclide concentrations contained in the extraction liquids are presented in [Bq/l] and their recalculations into portions of the initial dry mass [Bq/kg] as well. Furthermore, the respective relative dissolution portion is given in [%] and the errors of the gamma-spectrometry measurements for each extract are shown. Here, the results are presented in column diagrams for better understanding.

5.2.1 Phosphate industry

The phosphate ore sample R-PO-1 is characterised by an almost complete dissolution of ^{226}Ra in frame of the BCR procedure, whereas the other relevant radionuclides remained in the

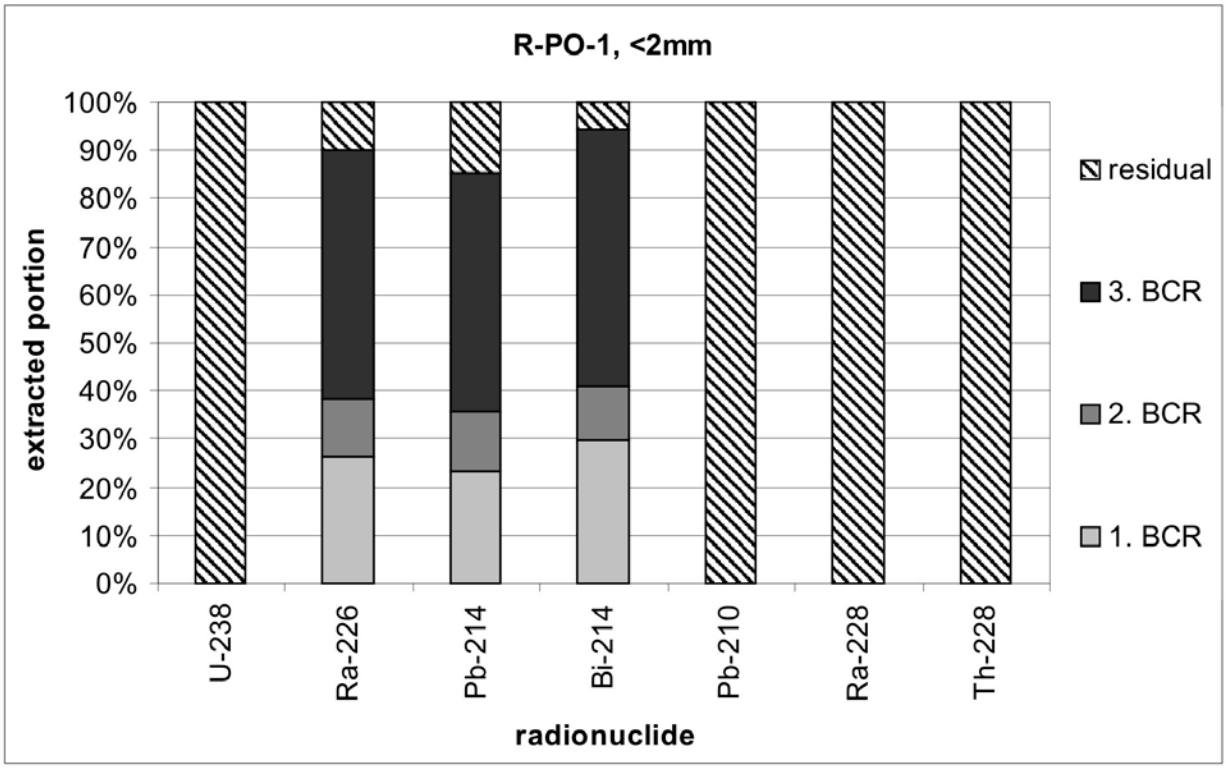

Fig. 5-17: Radionuclide fractions dissolved by BCR-procedure from the phosphate ore R-PO-1, <2mm.

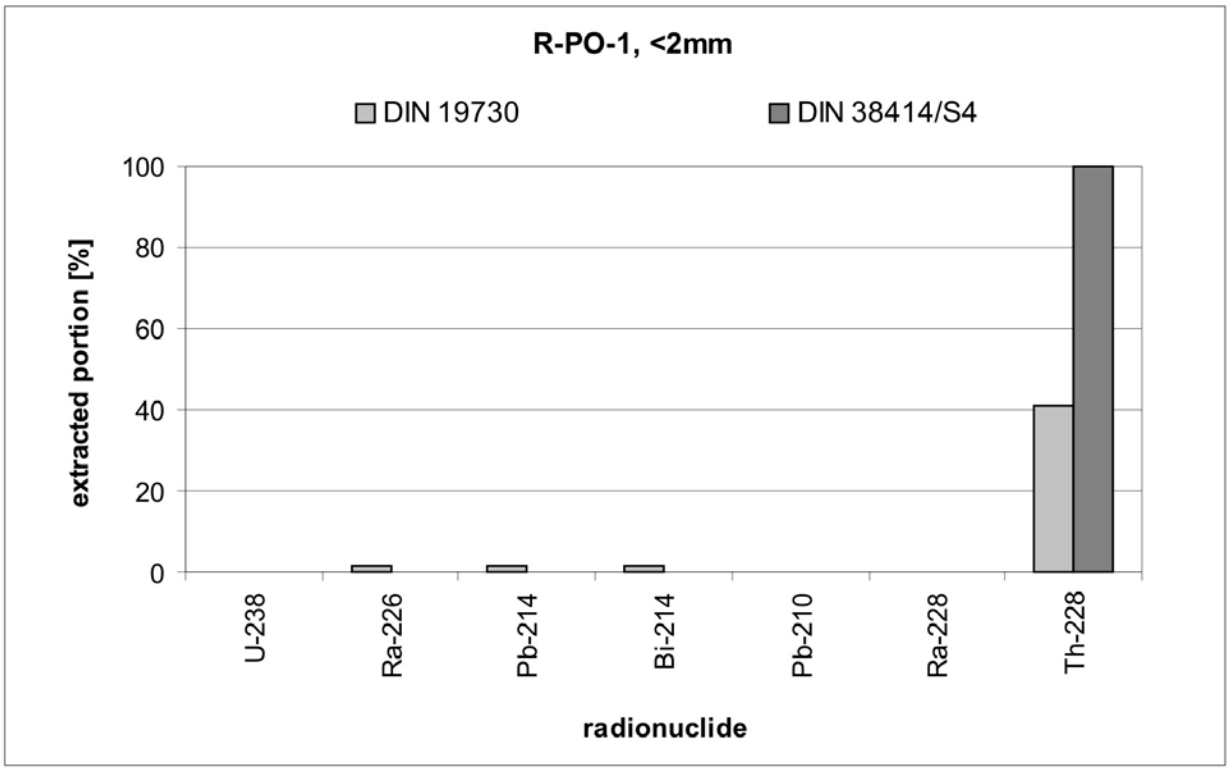

Fig. 5-18: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the phosphate ore R-PO-1, <2mm.

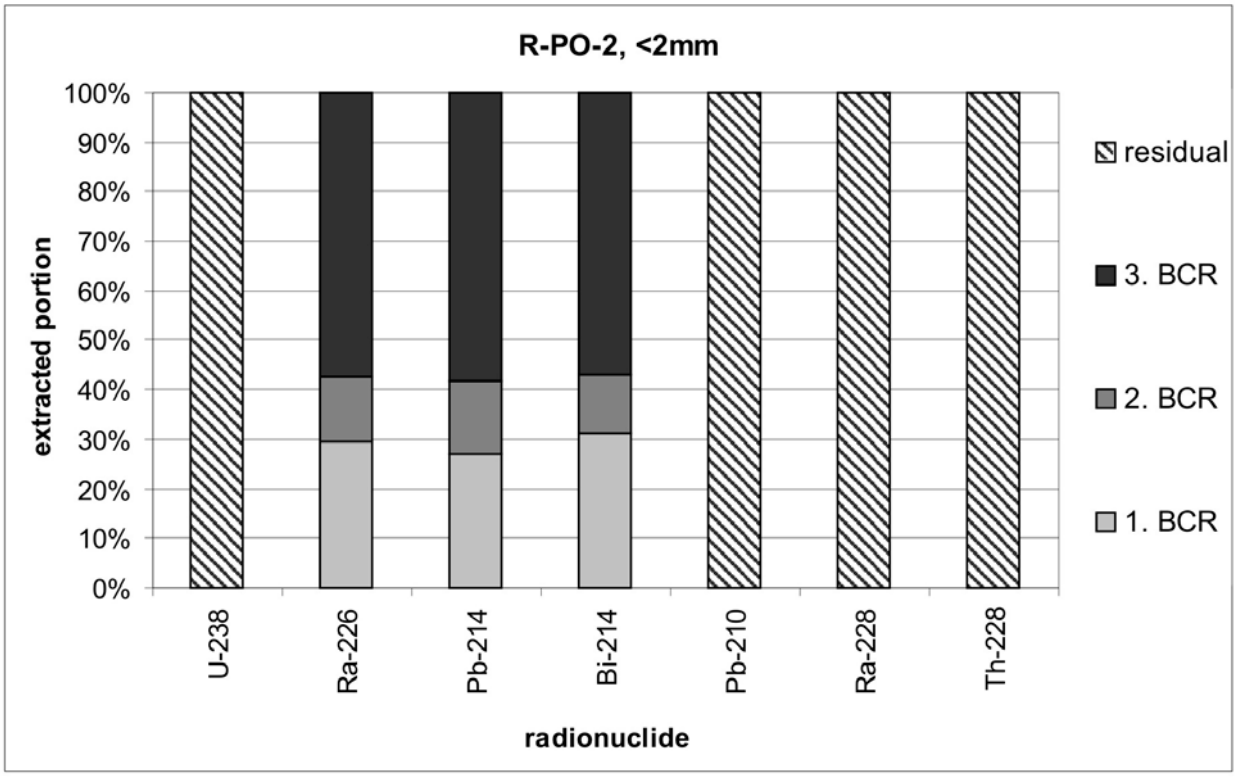

Fig. 5-19: Radionuclide fractions dissolved by BCR-procedure from the phosphate ore R-PO-2, <2mm.

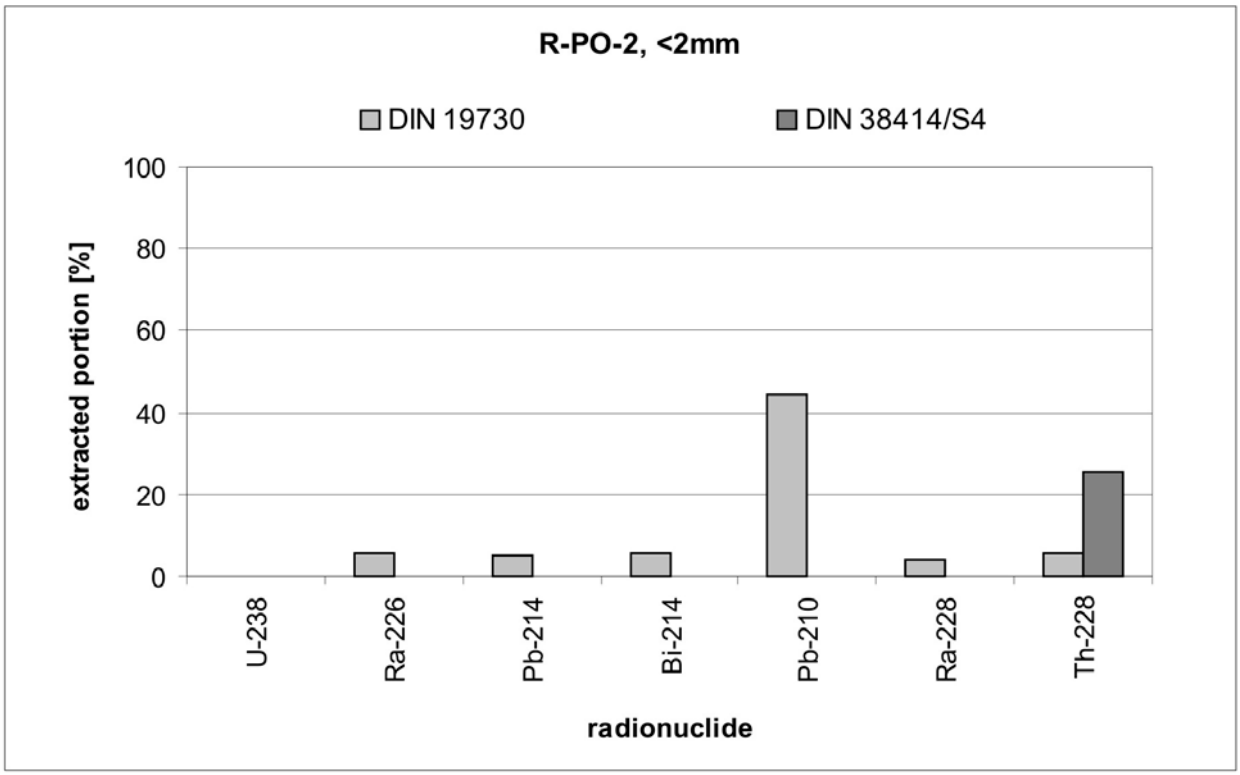

Fig. 5-20: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the phosphate ore R-PO-2, <2mm.

solid material (fig. 5-17). ^{226}Ra is bound in easily exchangeable state by 26%, a small amount of 12% is bound to manganese and iron oxides and the by far most, 52%, is bound to sulphides; the rest of 10% remained in the residual. The leaching procedures representing the water and plant

available fractions show a differentiated picture: ^{226}Ra remained almost complete in the solid material and ^{238}U, ^{210}Pb and ^{228}Ra were not detected (fig. 5-18). The only exception is ^{228}Th, which can be proven in both cases: all the initial amount was leached by water, up to 40% are plant available. These radionuclide characteristics also occur in the second phosphate ore sample R-PO-2. All the initial ^{226}Ra content was dissolved in frame of the BCR extraction procedure in same portions as in R-PO-1 (1. BCR: 29%, 2. BCR: 13%, 3. BCR: 58%) and also no other radionuclide was detected in the extraction liquids (fig. 5-19). The water solubility was just proven for ^{228}Th up to 24%, which is less compared with R-PO-1, and small amounts of ^{226}Ra, ^{228}Ra and ^{228}Th, roughly 5% each, were determined to be plant available (fig. 5-20). One exception is given by ^{210}Pb, which was leached to almost 50% and this is the main difference compared with R-PO-1.

The waste material phosphogypsum provides ^{226}Ra completely in frame of the BCR extraction procedure (fig. 5-21). 48% of the initial content were solved by the first easily exchangeable step, 20% are bound in the reducible fraction and 32% are fixed in the oxidisable fraction. ^{238}U, ^{210}Pb, ^{228}Ra and ^{228}Th were not detected. As shown in fig. 5-22, almost all the ^{210}Pb content is plant available beside 10% of the initial ^{228}Th. Also 38% of ^{228}Th were solved by water, the other radionuclides are not water soluble.

The final products P-F-1 and P-F-2, which are different fertiliser types, show also differentiated characteristics for their radionuclides' chemical type of bounding. The NPK-fertiliser (P-F-1) consists of ^{226}Ra, which is hardly exchangeable, only 4% were found in the 1. BCR fraction (fig. 5-23). The rest is of reducible and oxidisable state to almost same portions: 52% were found in the 2. and 44% in the 3. BCR fraction, nothing was left in the residual. The other radionuclides were not detected in any of the BCR's extraction liquids. The second product P-F-2, which is a PK-type fertiliser, provides 51% of the initial ^{226}Ra as easily exchangeable and 28% are fixed in the reducible respectively 21% in the oxidisable fraction (fig. 5-25). In addition, 83% of ^{210}Pb were solved by reducing reagents (2. BCR fraction) and 17% were found in the oxidisable fraction, which is a significant difference in comparison with P-F-1. Radionuclides of the ^{232}Th decay series were not detected due to their absence in the initial sample material (see chapter "5.1.1 Phosphate industry"), which also applies to both the DIN extraction procedures (fig. 5-26). The NPK-fertiliser (P-F-1) shows very low dimensions of ^{226}Ra as plant available (2%), but 17% of ^{210}Pb were leached (fig. 5-24), which is also in accordance with the PK-fertiliser (36%, fig. 5-26). ^{238}U and ^{228}Ra are not water or plant available, but ^{228}Th is completely dissoluted by water and up to 83% are available for plants (fig. 5-24). In case of P-F-2, uranium is the most important leachable radionuclide: it appears in the plant available (44%) and the water soluble fraction (26%) as well (fig. 5-26). 33% of ^{210}Pb was determined to be plant available, but nothing was leached by water. ^{226}Ra is hardly affected by both the extraction procedures: 1% is plant available and 3% are water soluble.

It can be summarised that all three material types occurring in frame of the fertiliser production do provide ^{226}Ra almost always completely in frame of the BCR extraction procedure, but it is hardly plant available and water soluble. In those fractions ^{210}Pb and ^{228}Th are the most important leachable radionuclides.

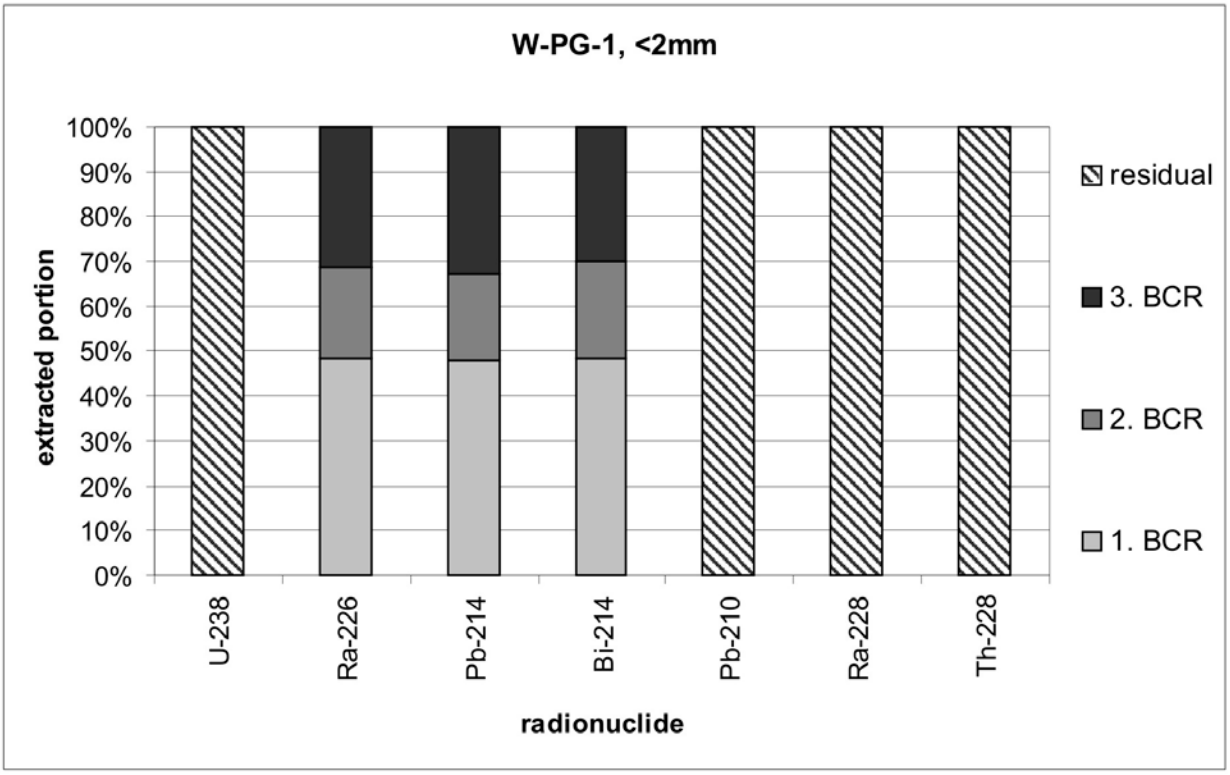

Fig. 5-21: Radionuclide fractions dissolved by BCR-procedure from the phosphogypsum W-PG-1, <2mm.

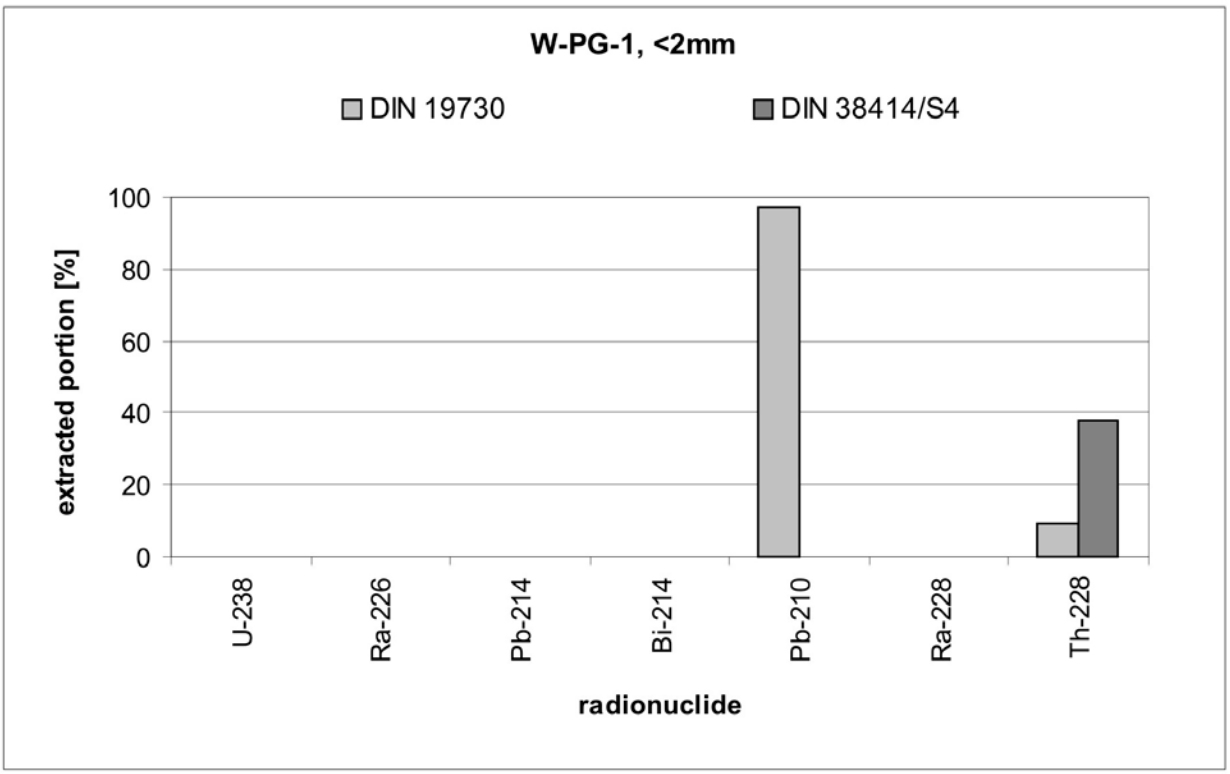

Fig. 5-22: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the phosphogypsum W-PG-1, <2mm.

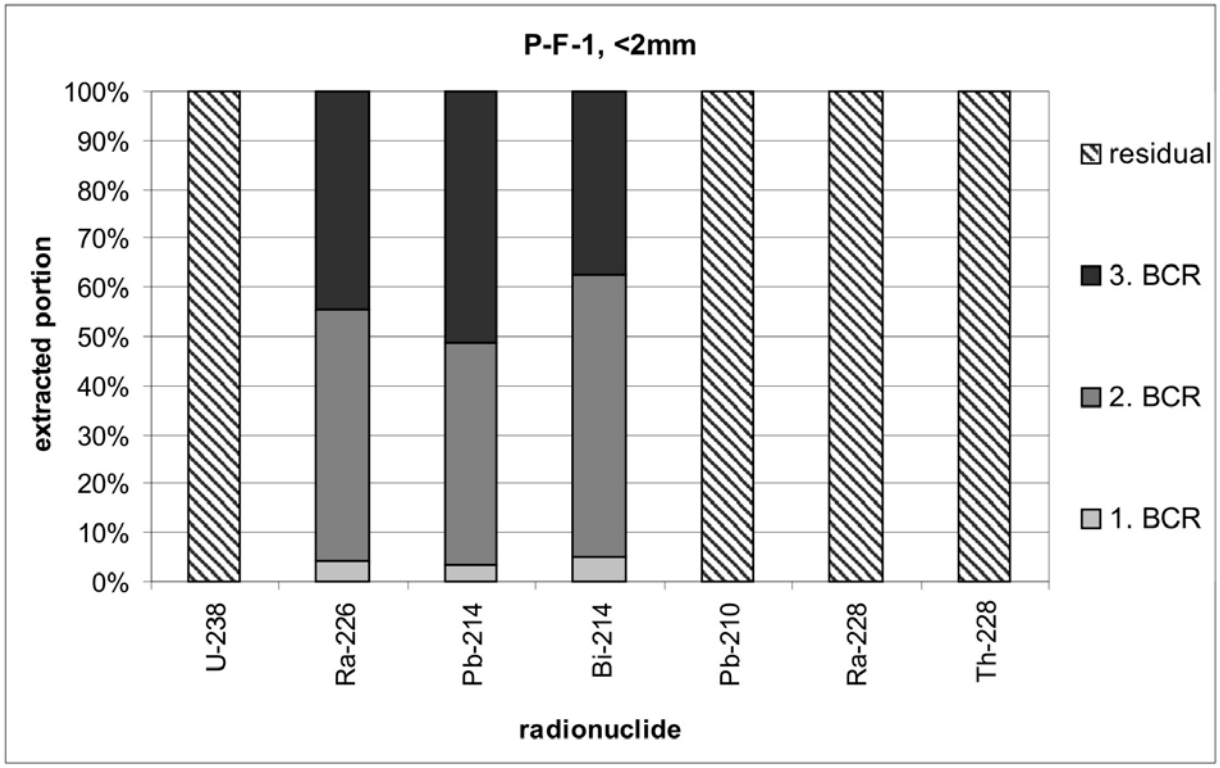

Fig. 5-23: Radionuclide fractions dissolved by BCR-procedure from the fertiliser P-F-1, <2mm.

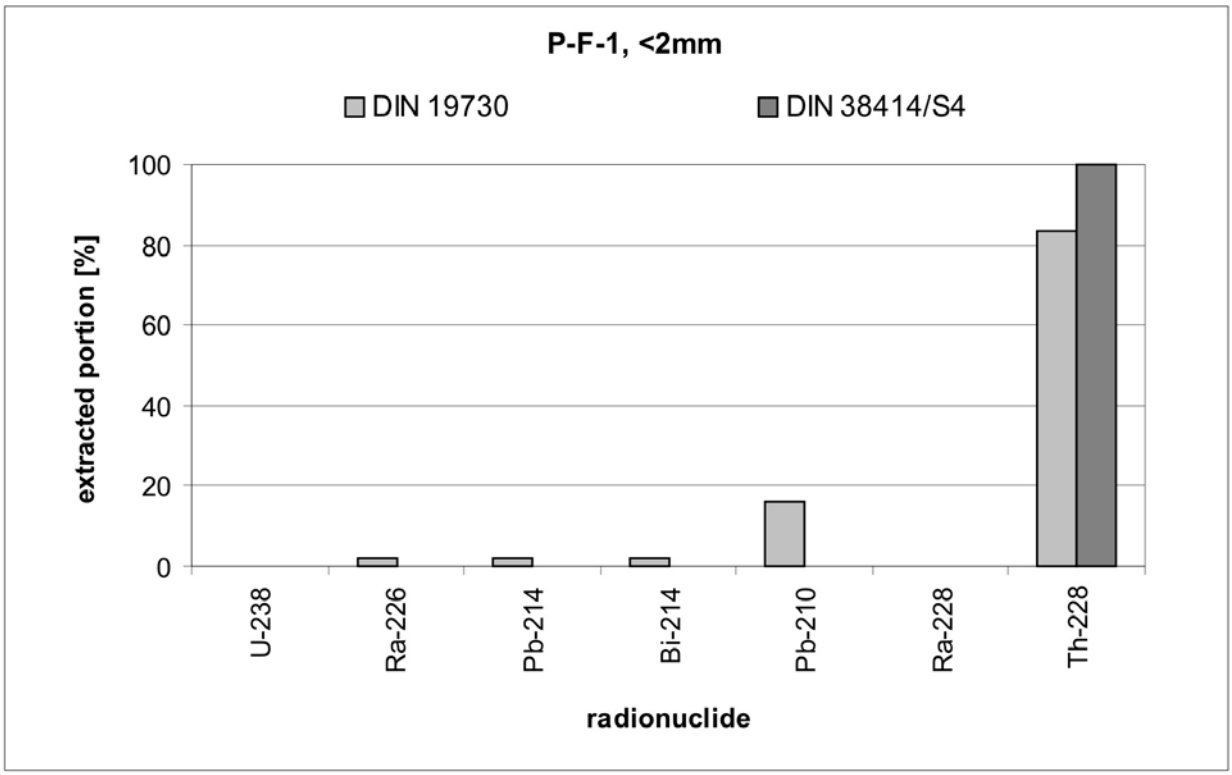

Fig. 5-24: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the fertiliser P-F-1, <2mm.

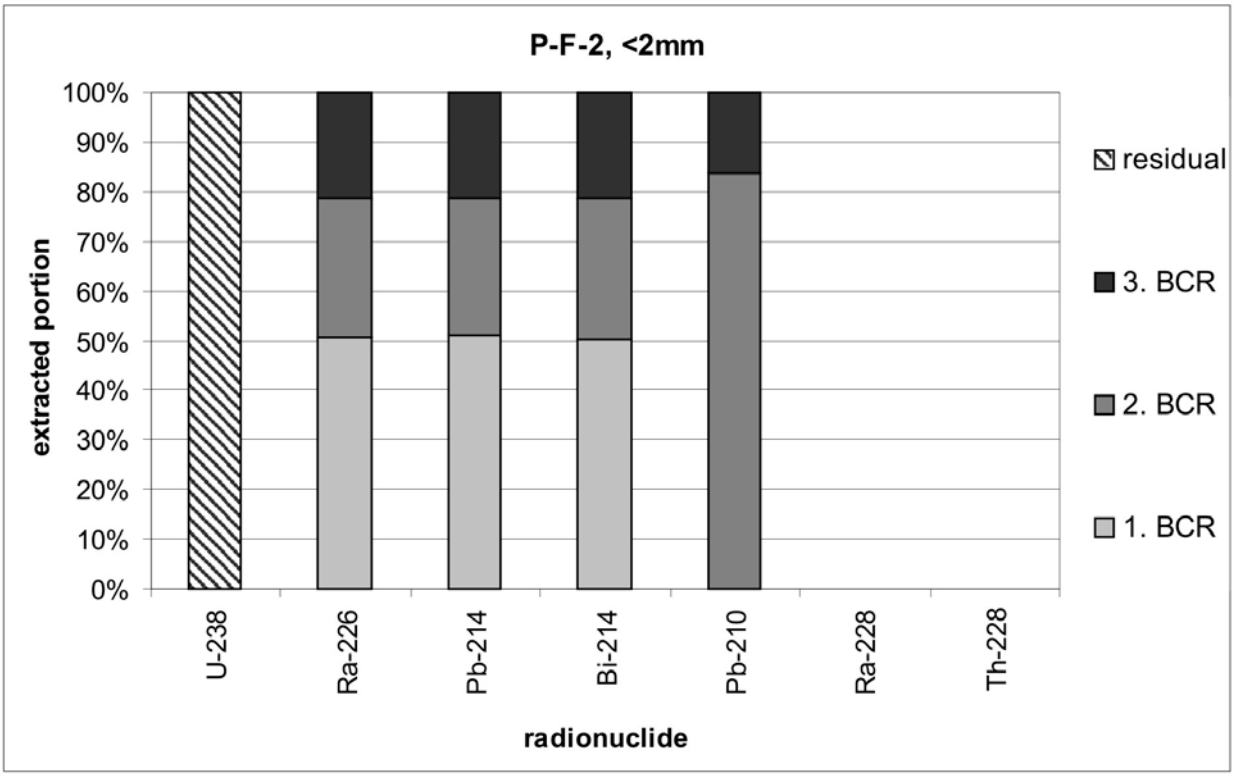

Fig. 5-25: Radionuclide fractions dissolved by BCR-procedure from the fertiliser P-F-2, <2mm.

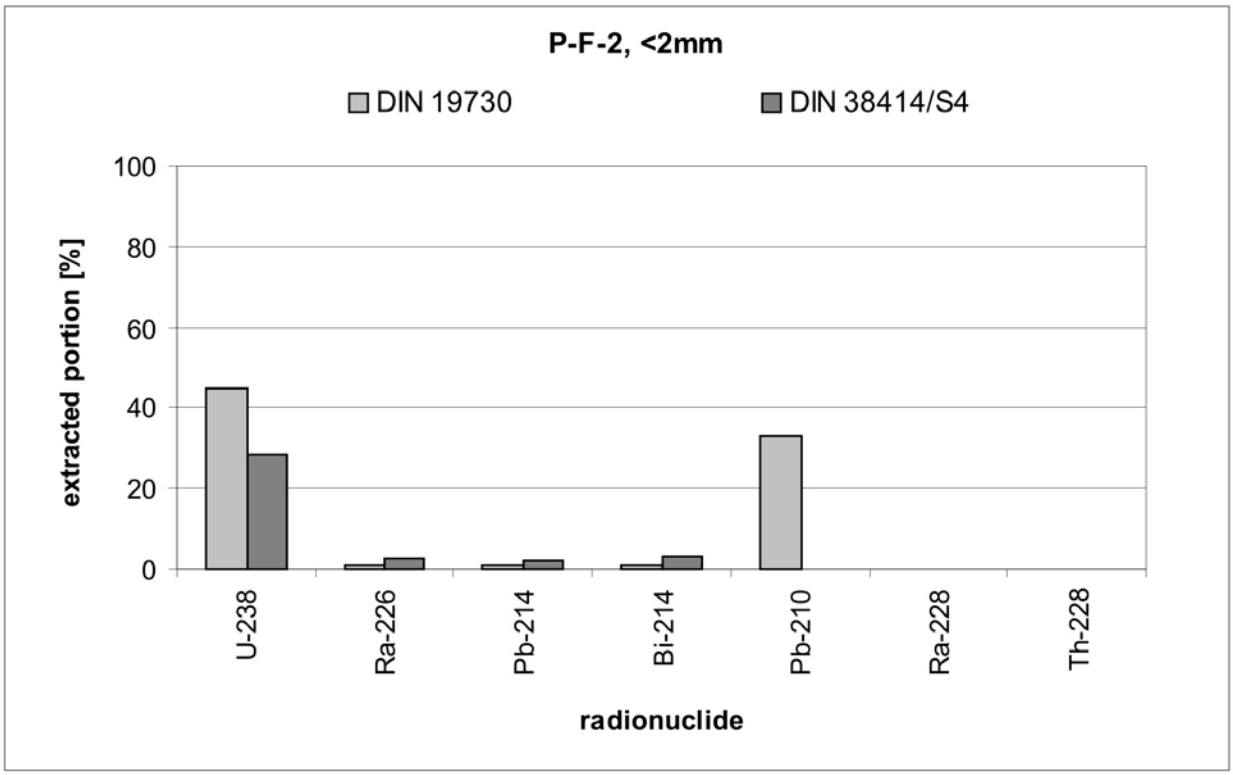

Fig. 5-26: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the fertiliser P-F-2, <2mm.

5.2.2 Aluminium industry

Both the aluminium ores R-AO-1 and R-AO-2 and the waste red sludge were delivered in sufficient volumes to separate them into the fractions <2mm and <0.1mm each. The first sample

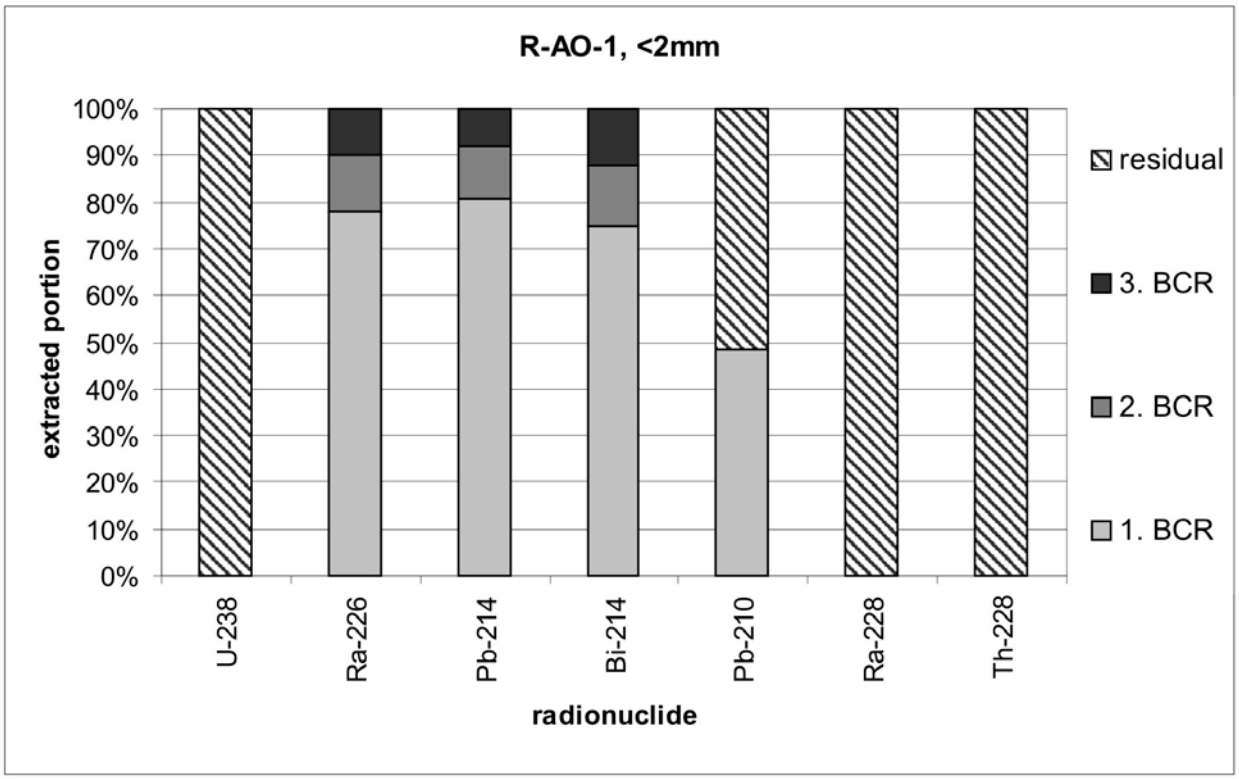

Fig. 5-27: Radionuclide fractions dissolved by BCR-procedure from the aluminium ore R-AO-1, <2mm.

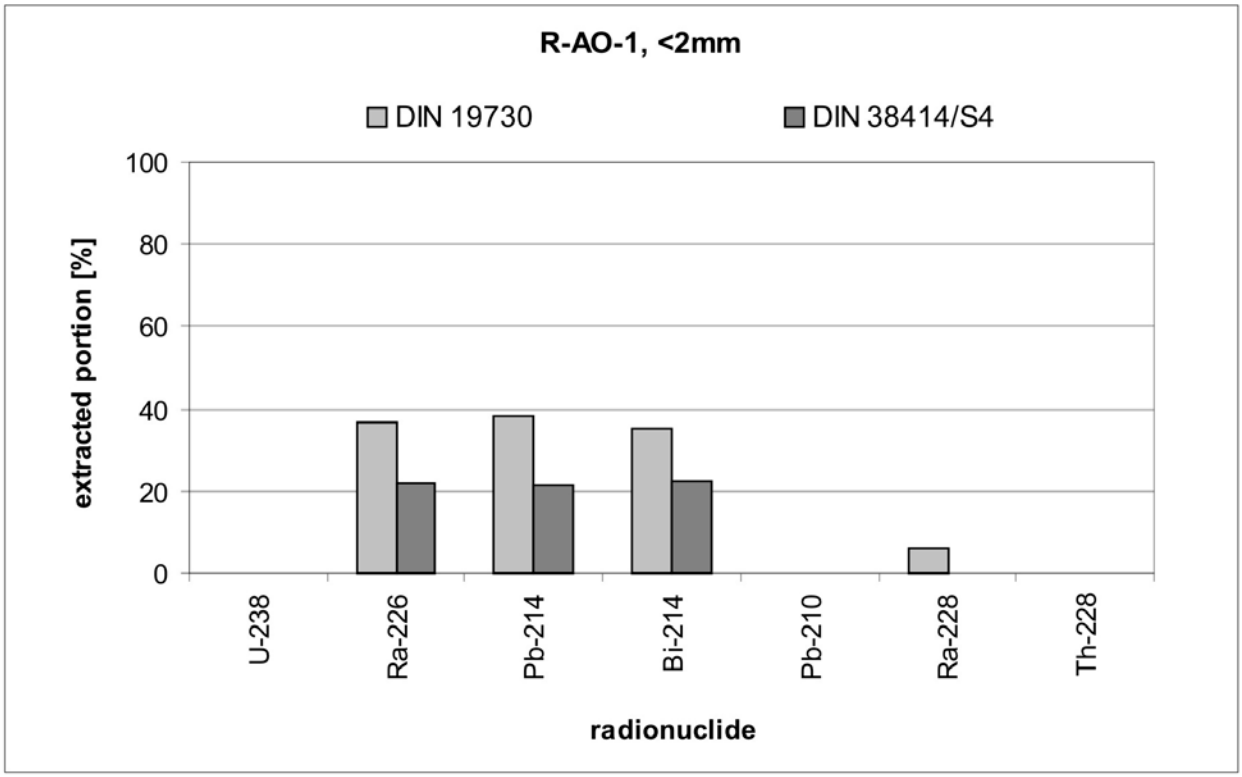

Fig. 5-28: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the aluminium ore R-AO-1, <2mm.

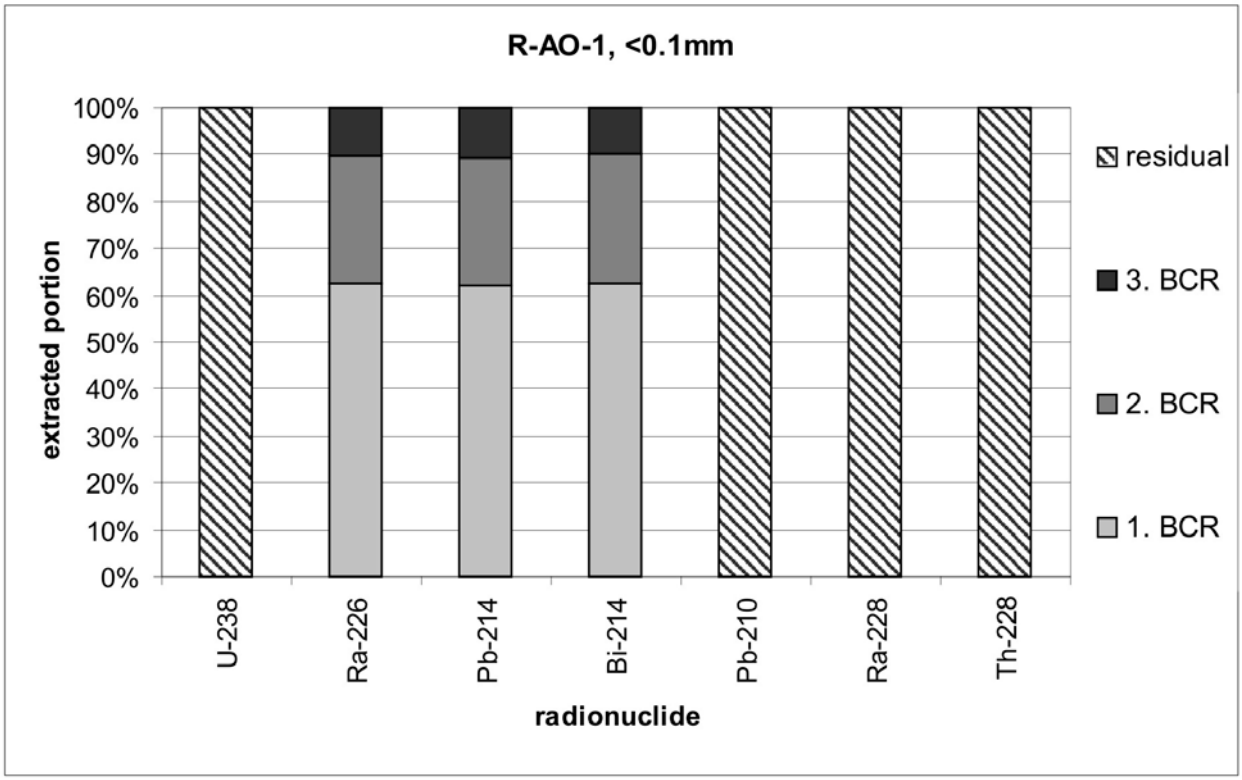

Fig. 5-29: Radionuclide fractions dissolved by BCR-procedure from the aluminium ore R-AO-1, <0.1mm.

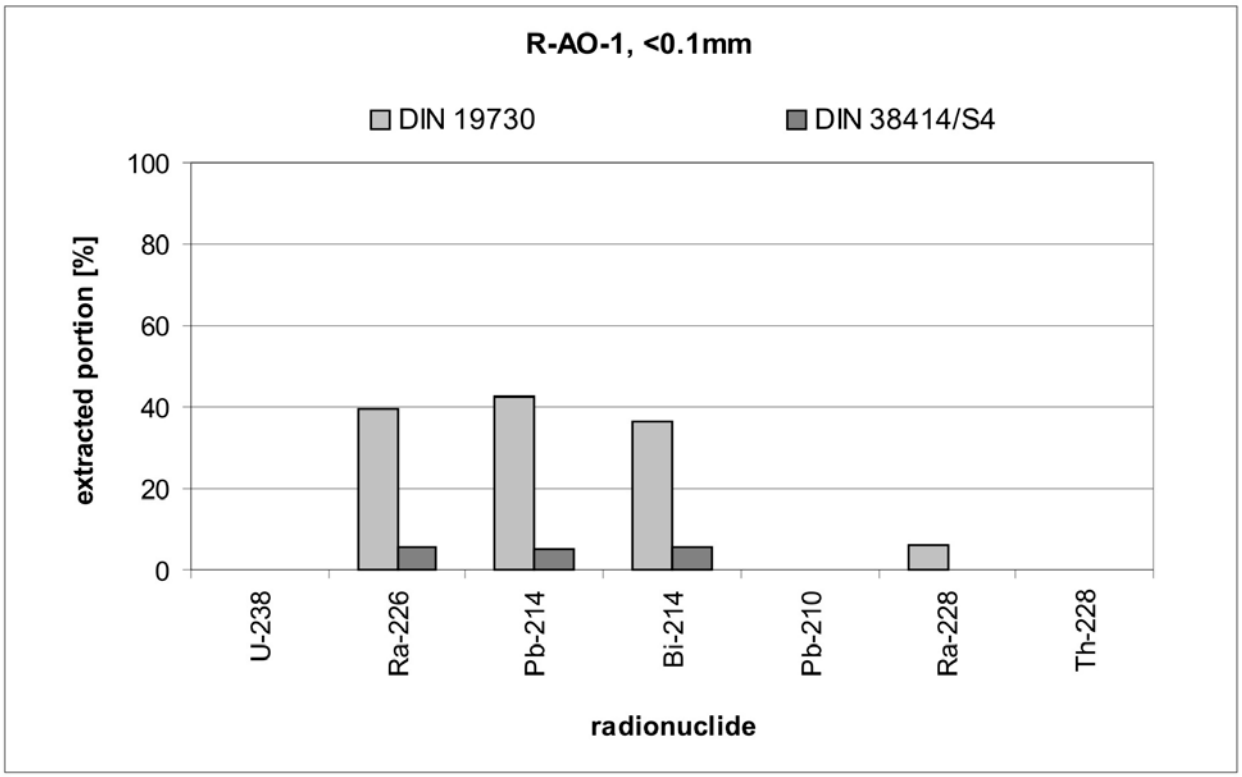

Fig. 5-30: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the aluminium ore R-AO-1, <0.1mm.

R-AO-1, <2mm, provides ^{226}Ra and ^{210}Pb in the easily exchangeable fraction in dimensions of 78% respectively 49%, other radionuclides were not leached within the whole BCR procedure (fig. 5-27). Further on, only ^{226}Ra is proven in the reducible (12%) and oxidisable (10%) fraction.

The milled fraction <0.1mm shows a similar picture (fig. 5-29): the only dissoluted radionuclide is ^{226}Ra present of 62% in the 1. BCR fraction, 27% in the 2. BCR and 11% in the 3. BCR fraction. This well accordance is also valid for the plant availability. The fraction <2mm leads to a plant available ^{226}Ra portion of 37% (fig. 5-28), in the fraction <0.1mm 39% are plant available (fig. 5-30) and ^{228}Ra was extracted by 8% each, whereas the other radionuclides were not affected. The only deviation concerns the dimensions of the leached amounts of ^{226}Ra by water: in the <2mm fraction 22% (fig. 5-28) were detected and in the <0.1mm 8% (fig. 5-30) are present. This radium isotope is the only water soluble radionuclide. A first conclusion is that the grain size does not influence the mobilisation potential of ^{226}Ra being stored in R-AO-1 significantly apart from water solubility.

The second aluminium ore sample R-AO-2 is also characterised by a similar radionuclide behaviour within both grain size fractions. The fraction <2mm leads to 56% dissoluted ^{226}Ra and 18% solved ^{210}Pb in the easily exchangeable extraction step (fig. 5-31), whereas the milled fraction does provide 40% ^{226}Ra and 26% ^{210}Pb (fig. 5-33). In both grain size fractions the other relevant radionuclides are not proven in any of the BCR extractants. ^{226}Ra is also present in the reducible fraction by 20% and in the oxidisable fraction by 24% having been extracted from the <2mm grain size (fig. 5-31). These ratios are shifted slightly in the grain size portion <0.1mm: 51% in the reducible fraction and 9% in the oxidisable fraction (fig. 5-33). The amount of ^{210}Pb being bound to manganese and iron oxides behaves similarly in both grain sizes: 10% in the fraction <2mm (fig. 5-31) and 11% in the fraction <0.1mm (fig. 5-33), both the 3. BCR liquids do not contain any lead. In contrast, 24% of the initial ^{226}Ra content can be found in the oxidisable fraction from the <2mm grain size (fig. 5-31) respectively 9% from the <0.1mm grain size (fig. 5-33). The plant availability just concerns both the radium isotopes, which were dissoluted in same dimensions from both grain size fractions: 38% of ^{226}Ra and 8% of ^{228}Ra from <2mm material (fig. 5-32), and 39% of ^{226}Ra and 6% of ^{228}Ra from the <0.1mm sample (fig. 5-34). The 1% ^{210}Pb dissoluted from the <0.1mm fraction is negligible. The radionuclides' water solubility is not of importance for both grain size fractions, only ^{226}Ra was leached to 2% from each (fig. 5-32 and 5-34). Since the radionuclides' leaching behaviours of both grain size fractions coincide very well, that influence can be taken for really poor as it is also pointed out for R-AO-1.

As ascertained for both raw materials, also the waste material sample W-RS-1 shows similar radionuclides' leaching behaviours for both grain size fractions. In each case, only ^{226}Ra was detected in the BCR's extraction liquids (with small differences in their dimensions) and in those of the DIN 19730 and DIN 38414/S4 extraction procedures as well. From the grain size material <2mm, 42% of the initial ^{226}Ra content is fixed in easily exchangeable state, 27% in the reducible and 31% in the oxidisable fraction (fig. 5-35). The <0.1mm fraction provides 24% for the 1. BCR step, 11% for the 2. BCR and the by far most of 63% for the 3. BCR step (fig. 5-37). In both cases, nothing was left in the residual. The radionuclide transfer into plants is not affected strongly, only 2% from the <2mm material's (fig. 5-36) and 5% from the <0.1mm sample's (fig. 5-38) ^{226}Ra content were dissoluted by that extraction. Also the water solubility is very similar in both grain sizes, but higher: 37% (fig. 5-36) and 33% (fig. 5-38) were determined to be water soluble.

In summary, it must be pointed out that the radionuclides' leaching behaviour of the aluminium raw materials and the waste red sludge as well are not significantly influenced by grain size differences. ^{226}Ra is always completely leached in frame of the BCR procedure, but the ratios

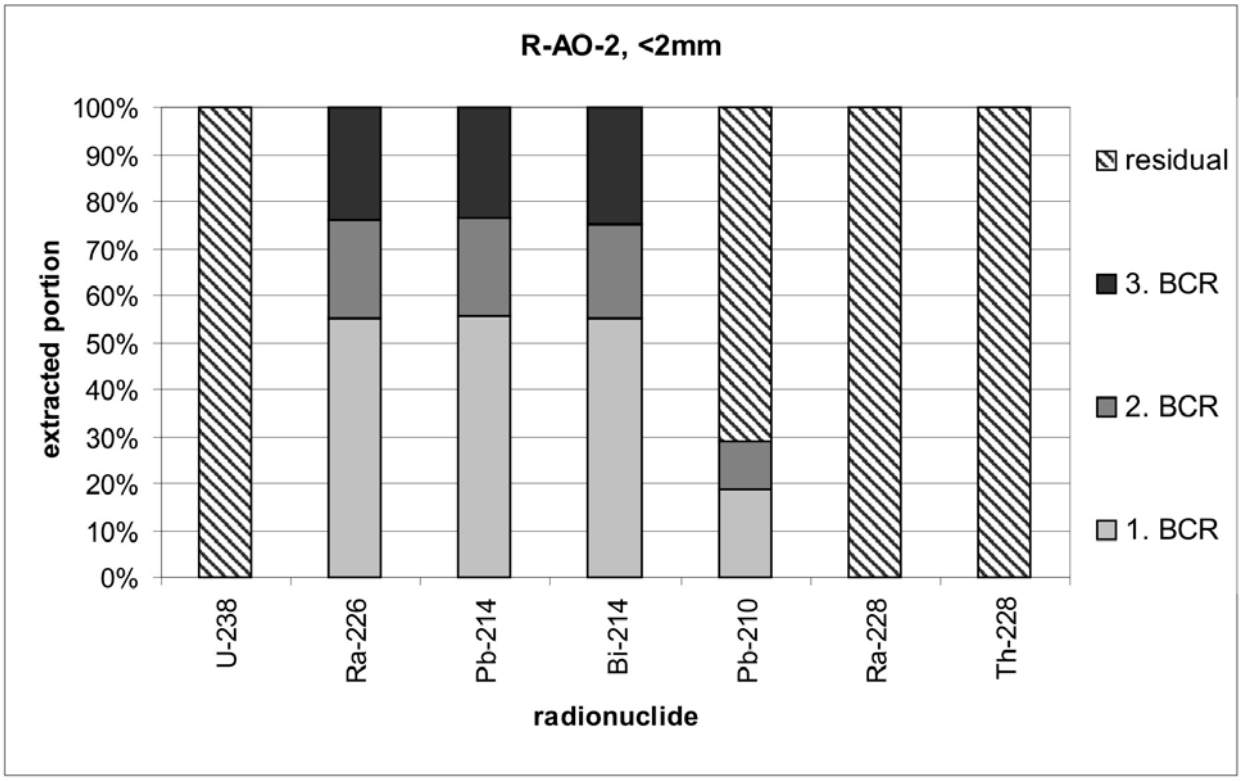

Fig. 5-31: Radionuclide fractions dissolved by BCR-procedure from the aluminium ore R-AO-2, <2mm.

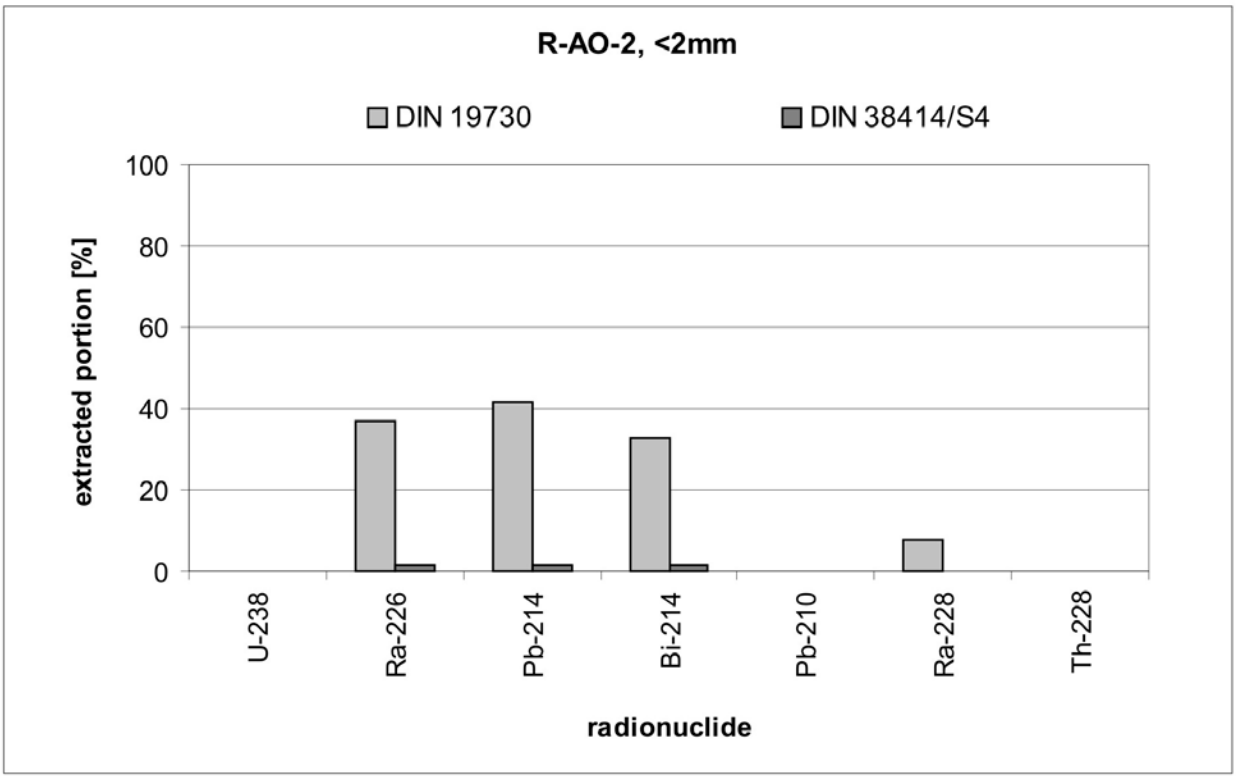

Fig. 5-32: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the aluminium ore R-AO-2, <2mm.

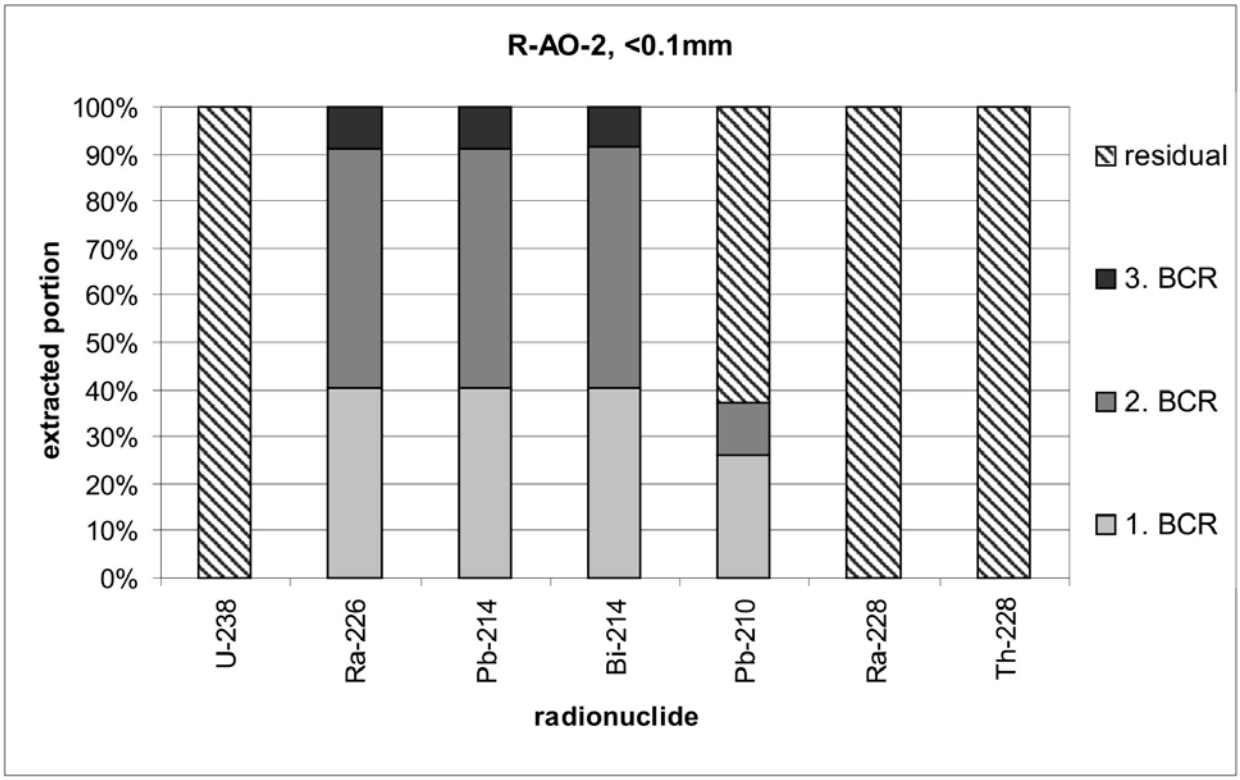

Fig. 5-33: Radionuclide fractions dissolved by BCR-procedure from the aluminium ore R-AO-2, <0.1mm.

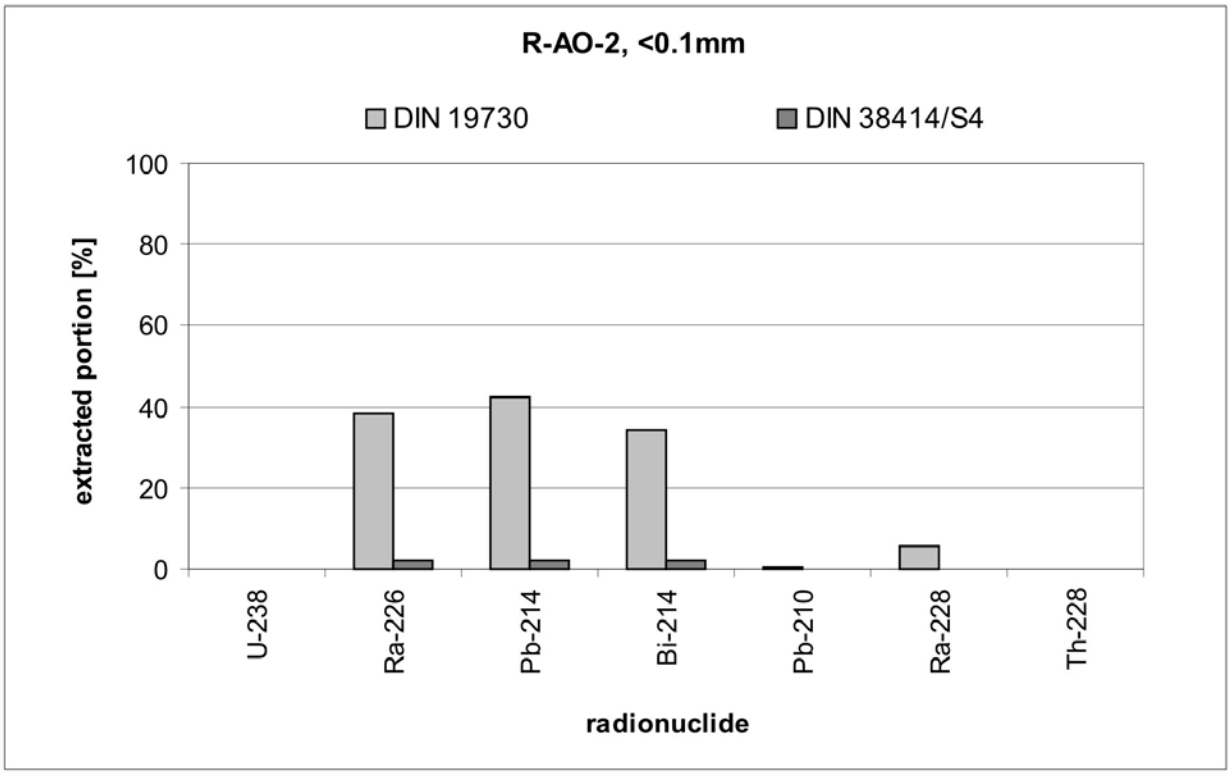

Fig. 5-34: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the aluminium ore R-AO-2, <0.1mm.

within the extraction steps can vary slightly. Also the plant available and water soluble extraction liquids do contain some ^{226}Ra in mentionable amounts of roughly 40%. If ^{210}Pb was leached, it is present in the the easily exchangeable and reducible fraction of the aluminium ores.

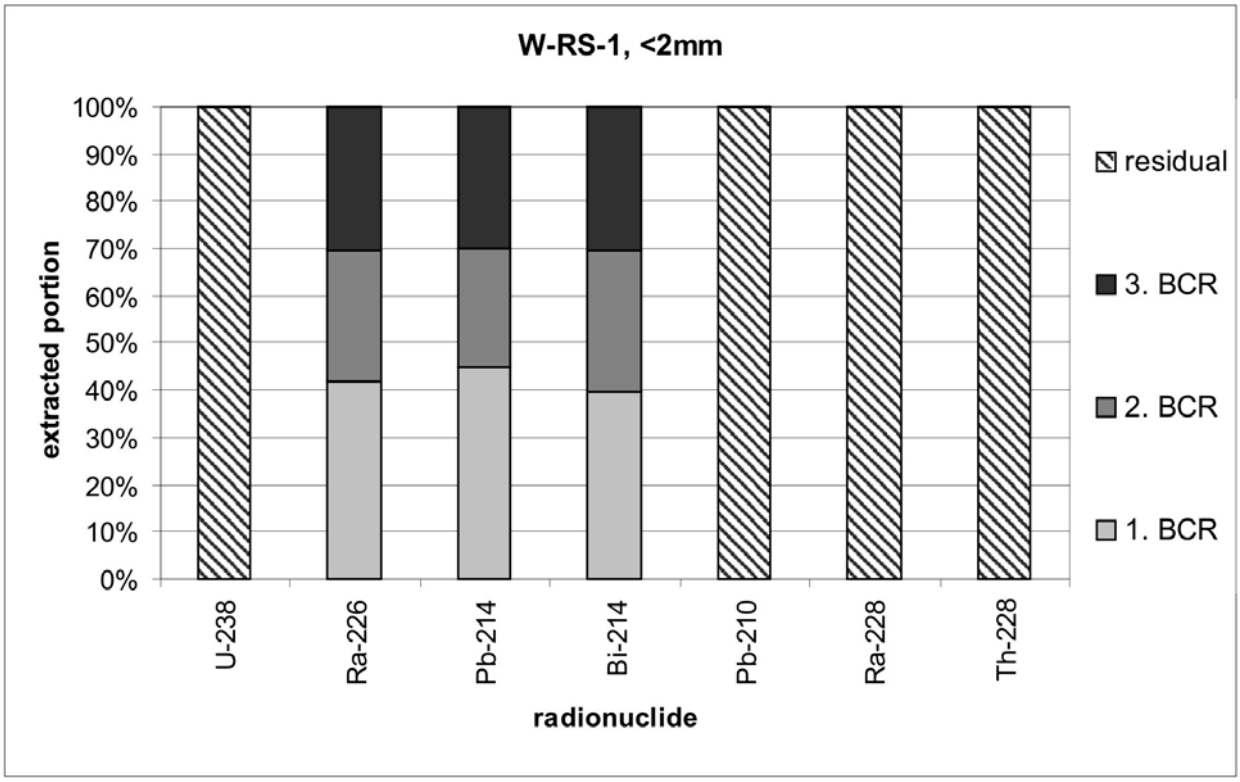

Fig. 5-35: Radionuclide fractions dissolved by BCR-procedure from the red sludge W-RS-1, <2mm.

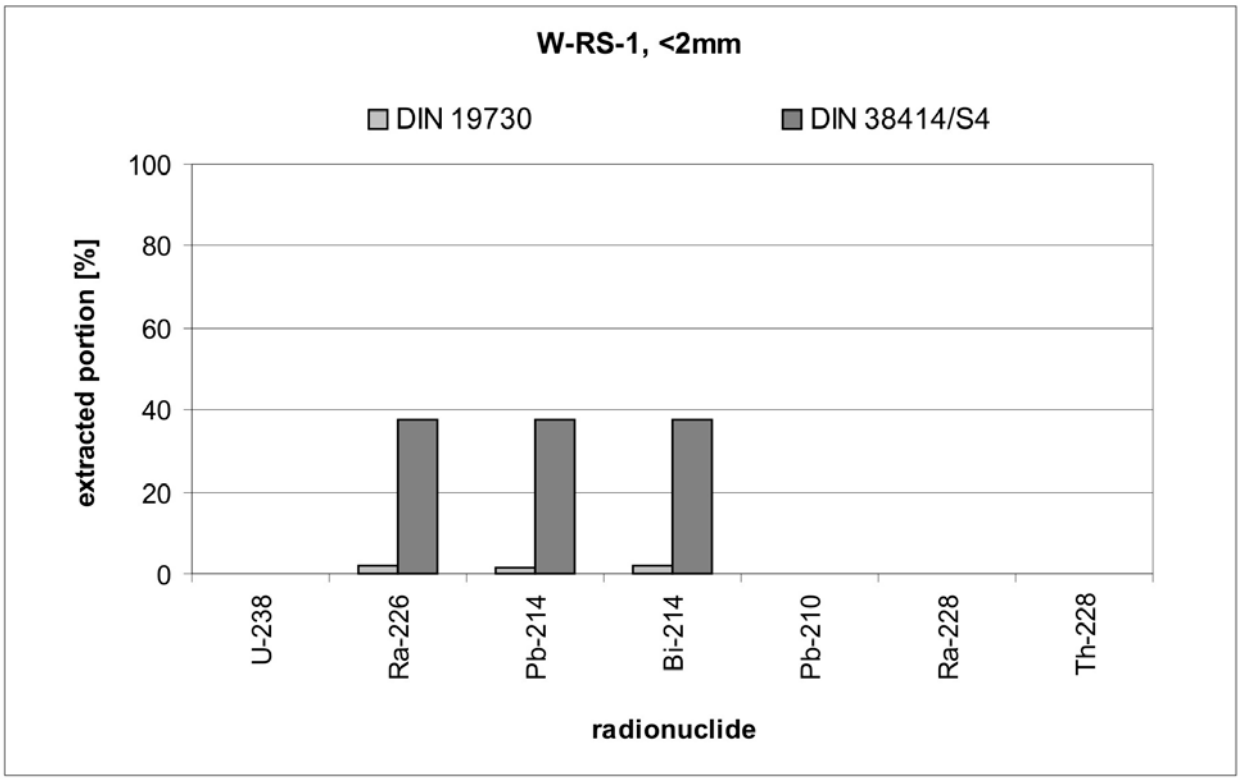

Fig. 5-36: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the red sludge W-RS-1, <2mm.

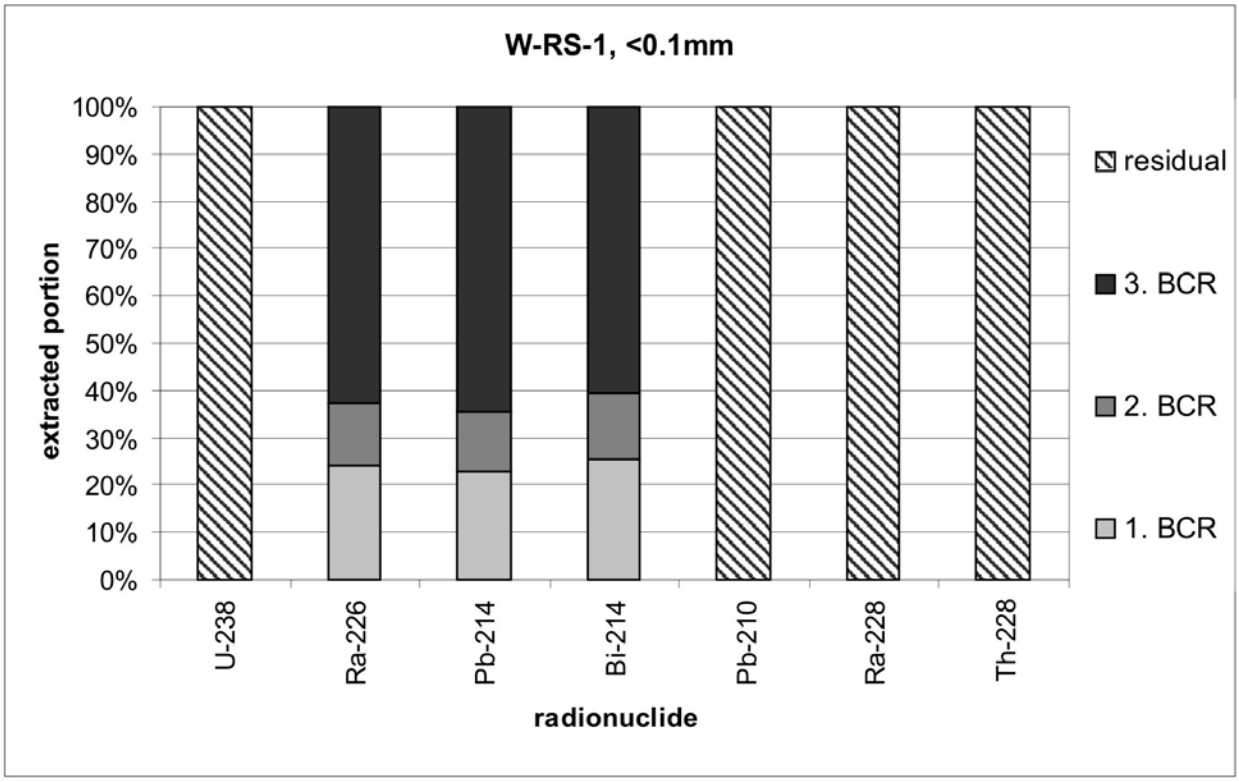

Fig. 5-37: Radionuclide fractions dissolved by BCR-procedure from the red sludge W-RS-1, <0.1mm.

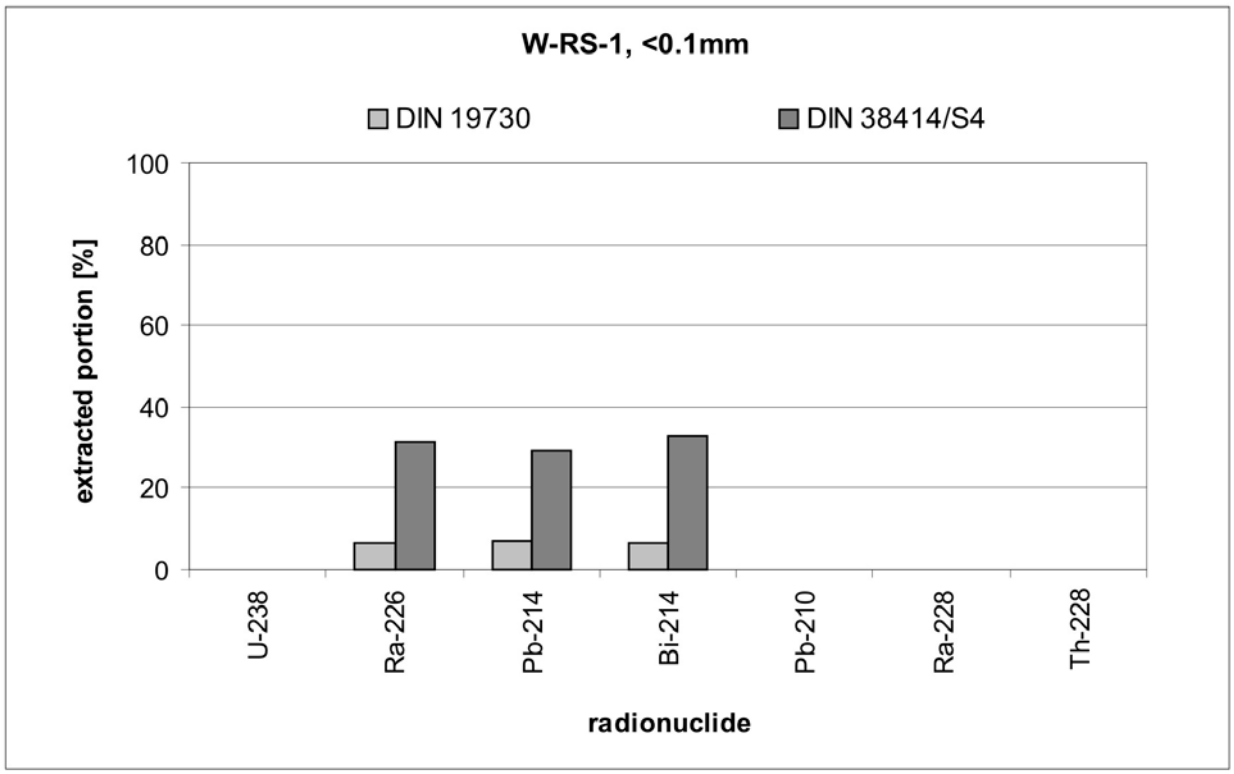

Fig. 5-38: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the red sludge W-RS-1, <0.1mm.

5.2.3 Refractory industry

The additively used raw material zircon sand does contain a few thousands Bq/kg of radionuclides from the uranium decay series (see chapter "5.1.3 Refractory industry"), but those are not really mobilisable under the chemical conditions being investigated within this thesis. In

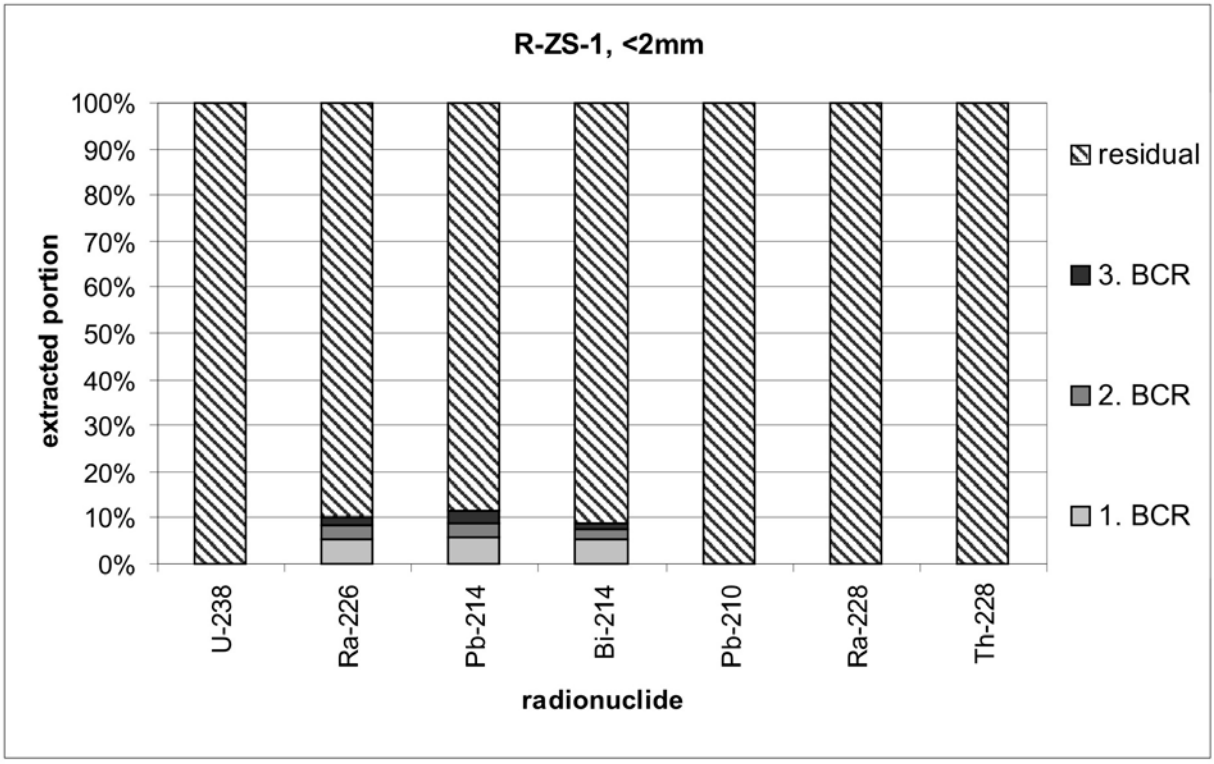

Fig. 5-39: Radionuclide fractions dissolved by BCR-procedure from the zircon sand R-ZS-1, <2mm.

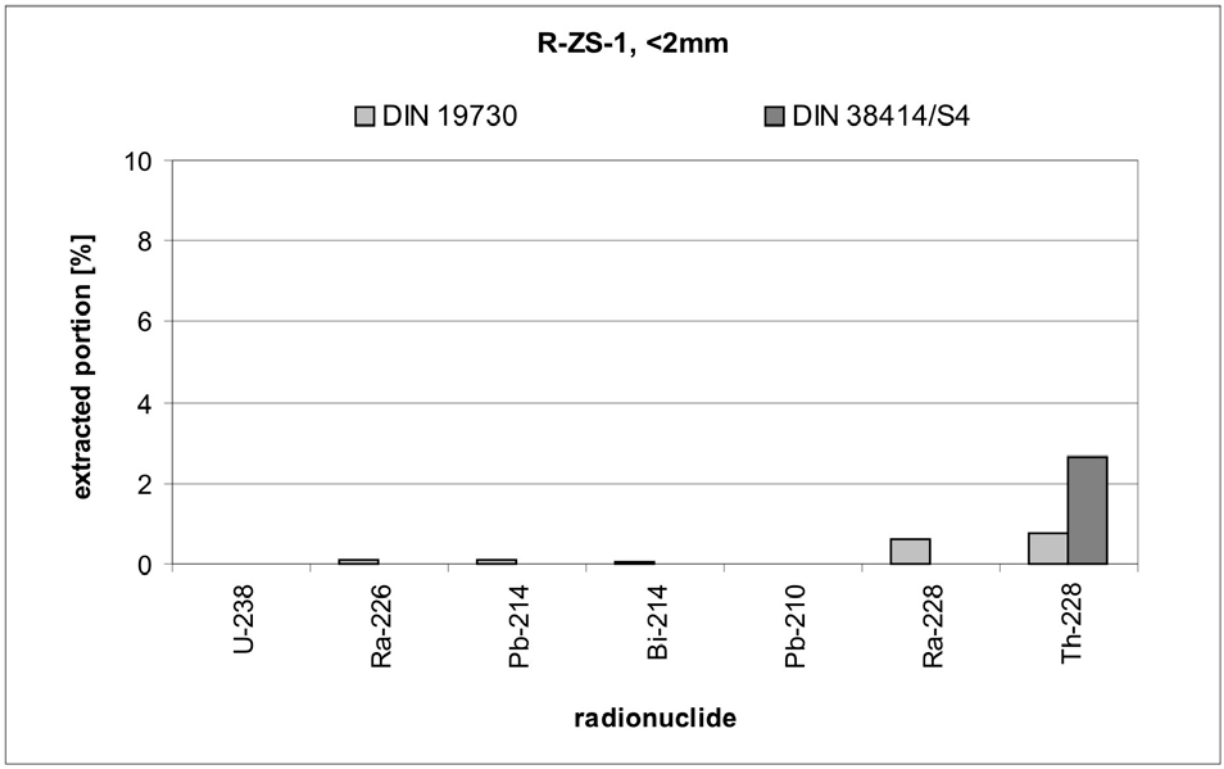

Fig. 5-40: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the zircon sand R-ZS-1, <2mm.

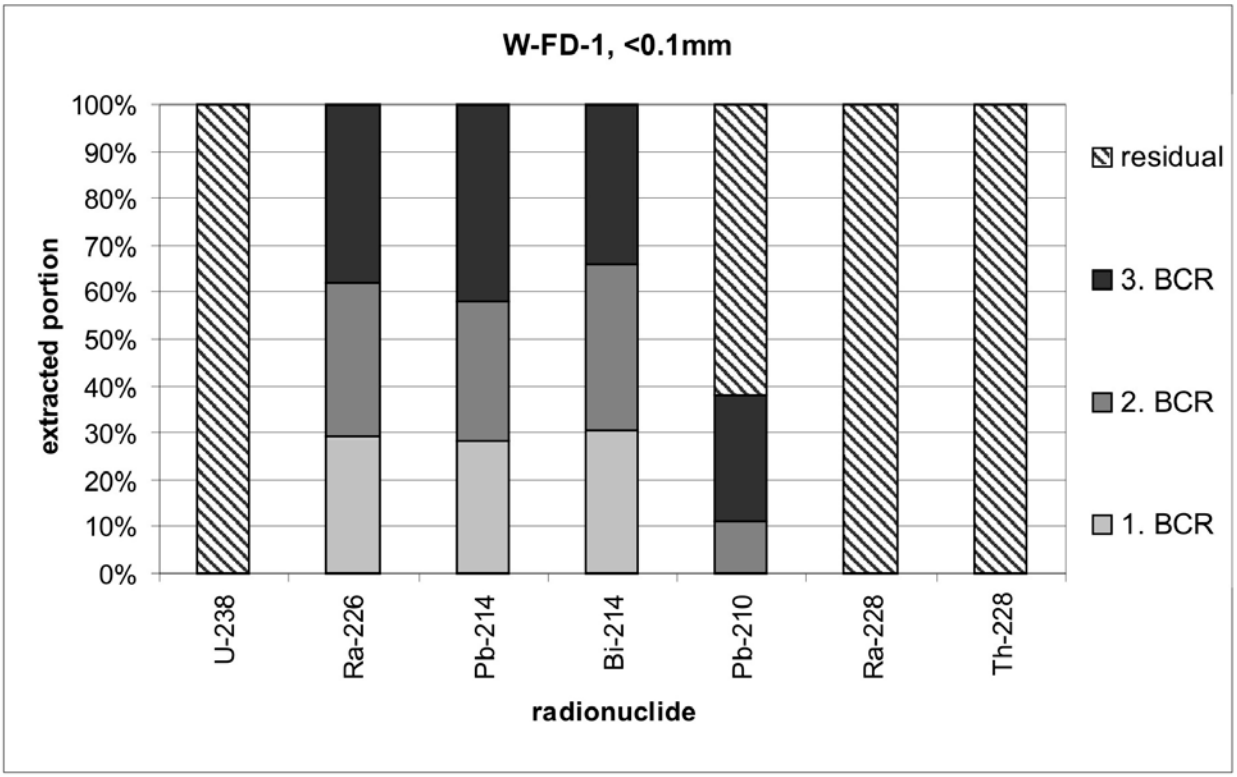

Fig. 5-41: Radionuclide fractions dissolved by BCR-procedure from the filter dust W-FD-1, <0.1mm.

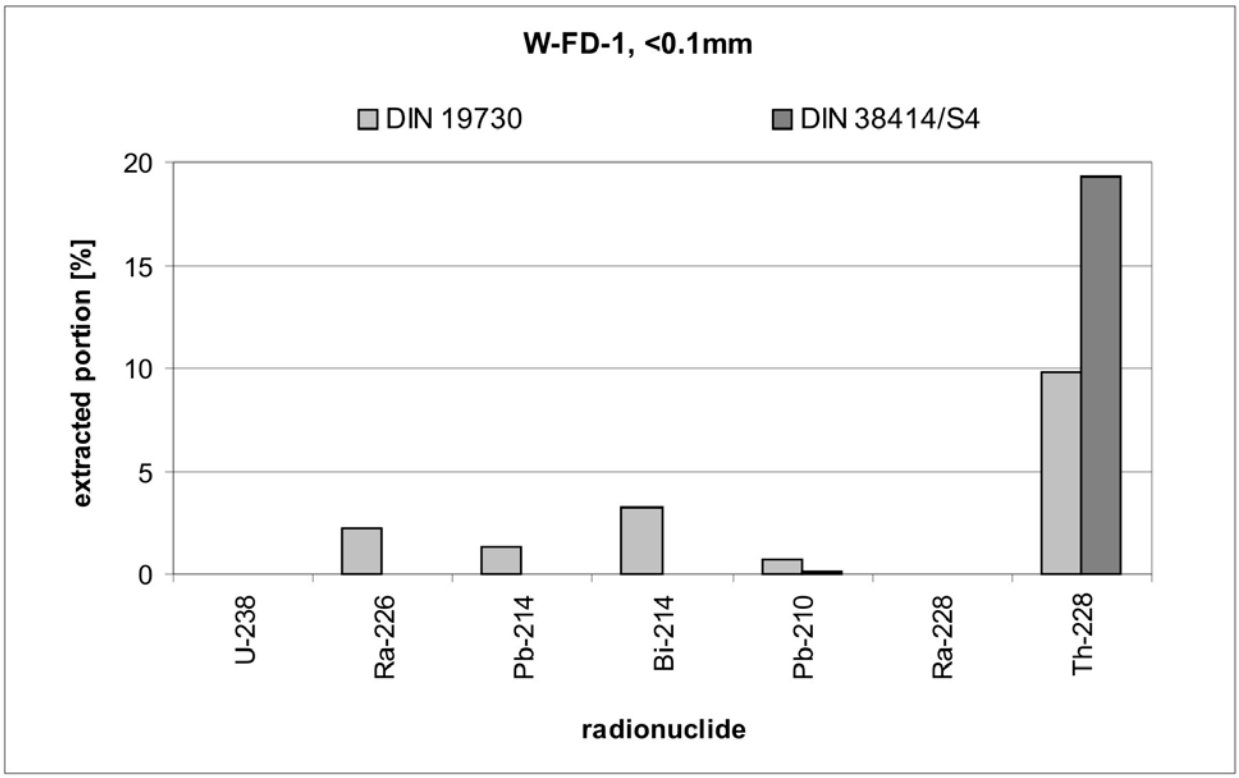

Fig. 5-42: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the filter dust W-FD-1, <0.1mm.

frame of the BCR extraction procedure, only ^{226}Ra can be proven in a total leached amount of 10% from the initial content (fig. 5-39), the distribution is 5% in 1. BCR, 3% in 2. BCR and 2% in the 3. BCR fraction. A similar picture is given for both the DIN extraction procedures, where only ^{228}Ra and ^{228}Th can be found ranging around 1% for the plant available and just ^{228}Th of 2%

for the water soluble fraction (fig. 5-40). Therefore, zircon sand can be taken for providing just small amounts of radionuclides by extracting according to BCR and the DIN procedures.

Within the BCR radionuclide fractions extracted from the waste material filter dust, which is of grain size <0.1mm due to its generation process, special attention must be paid to ^{210}Pb, because that shows the by far highest activity concentration of more than 100,000Bq/kg in the initial sample (see chapter "5.1.3 Refractory industry"). As shown in fig. 5-41, no lead was dissoluted by the easily exchangeable fraction, but 11% are bound to iron and manganese oxides and 27% to organic matter and sulphides. The total ^{226}Ra amount solved by the BCR extraction stands back due to the much lower initial activity concentration (less than 200Bq/kg). The distribution is as follows: 29% 1. BCR, 33% 2. BCR and 38% 3. BCR. ^{238}U, ^{228}Ra and ^{228}Th were not leached. The plant availability and water solubility concern both ^{210}Pb and ^{228}Th. The latter is present by 10% respectively 20%, but the 1% plant available ^{210}Pb (fig. 5-42) gets put into perspective by keeping in mind the immense initial activity concentration, the 2.5% ^{226}Ra portion is negligible.

Both the final products fused zirconia mullite show similar radionuclide leaching behaviour despite the fact that sample P-FZM-1 is of <2mm grain size and sample P-FZM-2 of <0.1mm. Sample 1 provides 40% ^{226}Ra in total being distributed among 14% easily exchangeable, 3% bound to manganese and iron oxides and 23% bound to organic matter and sulphides (fig. 5-43), sample 2 leads to 12% in total consisting of 3% 1. BCR, 7% 2. BCR and 2% 3. BCR (fig. 5-45). Another common characteristic is that no other radionuclide was leached each and also the plant availabilities and water solubilities stand back. The only mentionable extracted radionuclide is ^{228}Th, which occurs as water soluble by 6% (P-FZM-1, fig. 5-44) respectively 2% (P-FZM-2, fig. 5-46). In the plant available fraction ^{228}Ra (only P-FZM-2) and ^{228}Th can be found by 1% (fig. 5-44 and 5-46), the ^{226}Ra portions are not of importance.

It can besummarised that zircon sand does not provide mentionable amounts of radionuclides, but in case of filter dust attention must be focused on ^{210}Pb's leaching behaviour under oxidising conditions. Both the final products P-FZM-1 and P-FZM-2 results just in small amounts of leached radionuclides, mainly ^{226}Ra and ^{228}Th.

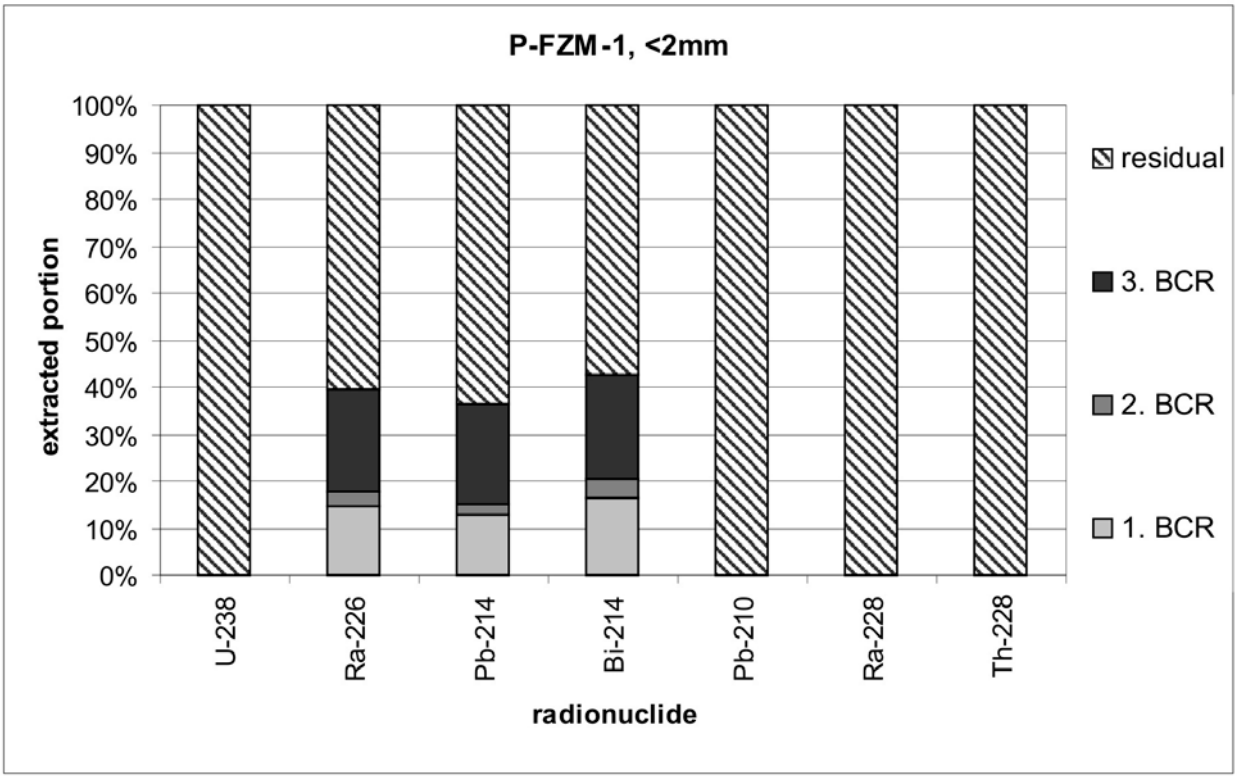

Fig. 5-43: Radionuclide fractions dissolved by BCR-procedure from the fused zirconia mullite P-FZM-1, <2mm.

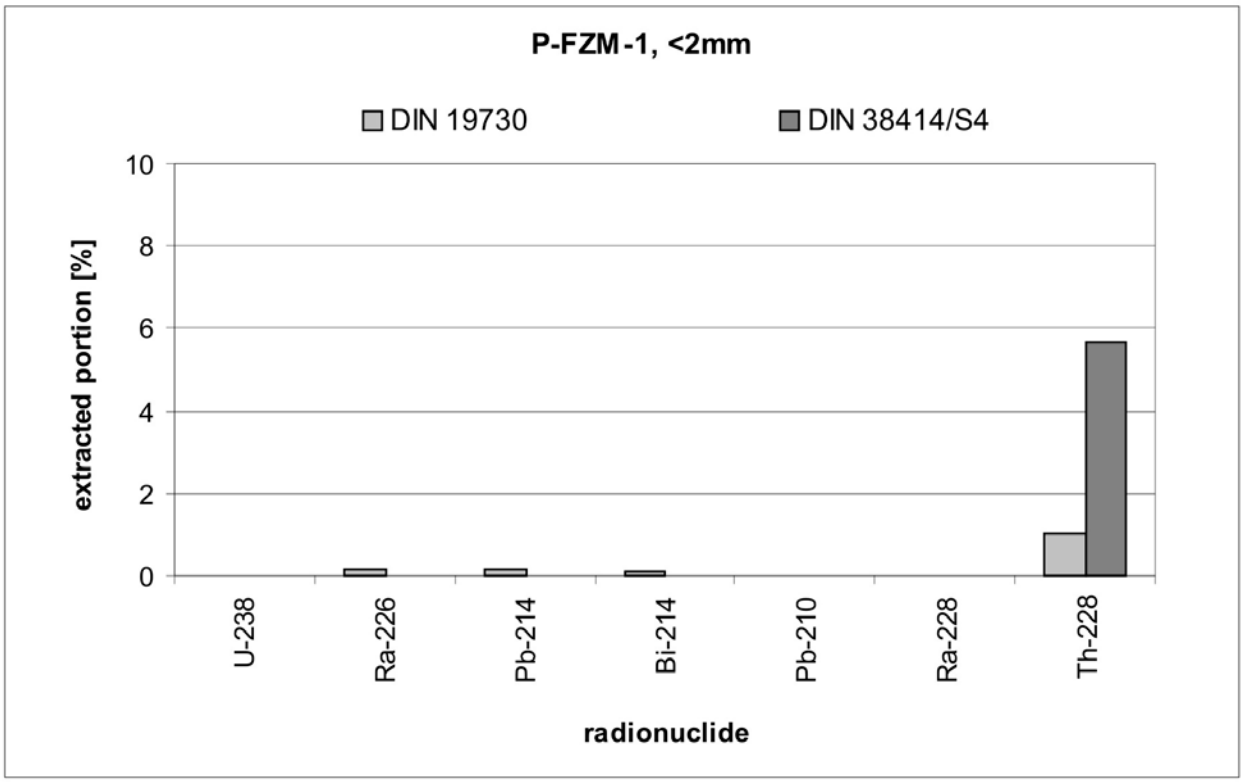

Fig. 5-44: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the fused zirconia mullite P-FZM-1, <2mm.

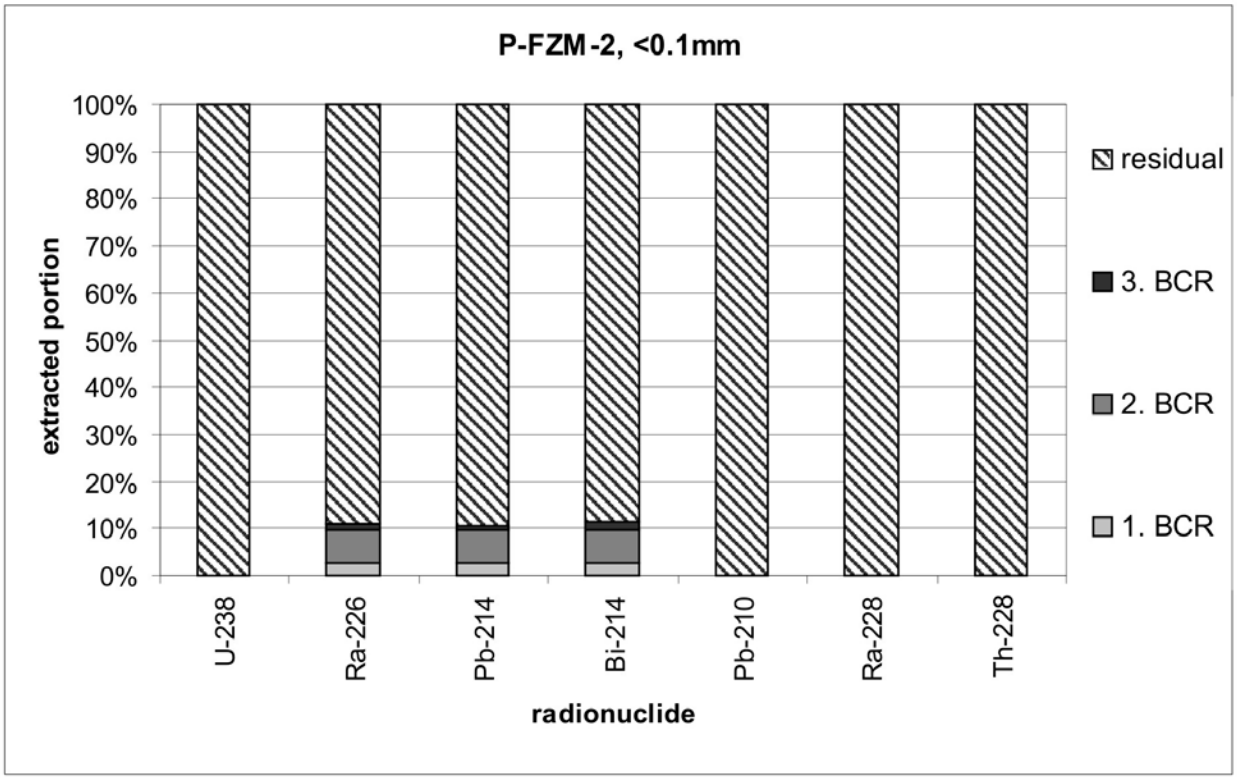

Fig. 5-45: Radionuclide fractions dissolved by BCR-procedure from the fused zirconia mullite P-FZM-2, <0.1mm.

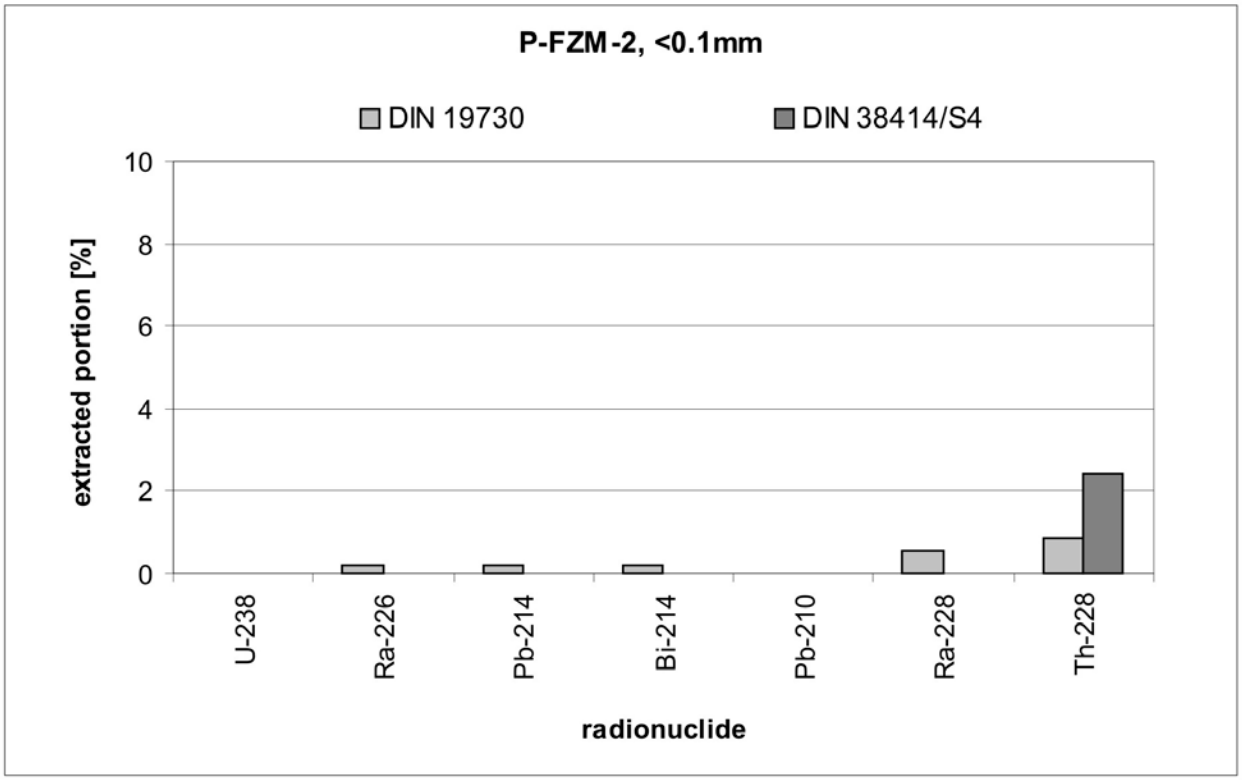

Fig. 5-46: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the fused zirconia mullite P-FZM-2, <0.1mm.

5.2.4 Crude oil exploitation

As obvious from fig. 5-47, the sludge sample W-SL-1, <2mm, especially provides ^{210}Pb in frame of the BCR extraction procedure, ^{226}Ra, ^{228}Ra and ^{228}Th stand back. 18% of the initial lead are bound in easily exchangeable state, 5% are fixed on iron and manganese oxides and 17% on

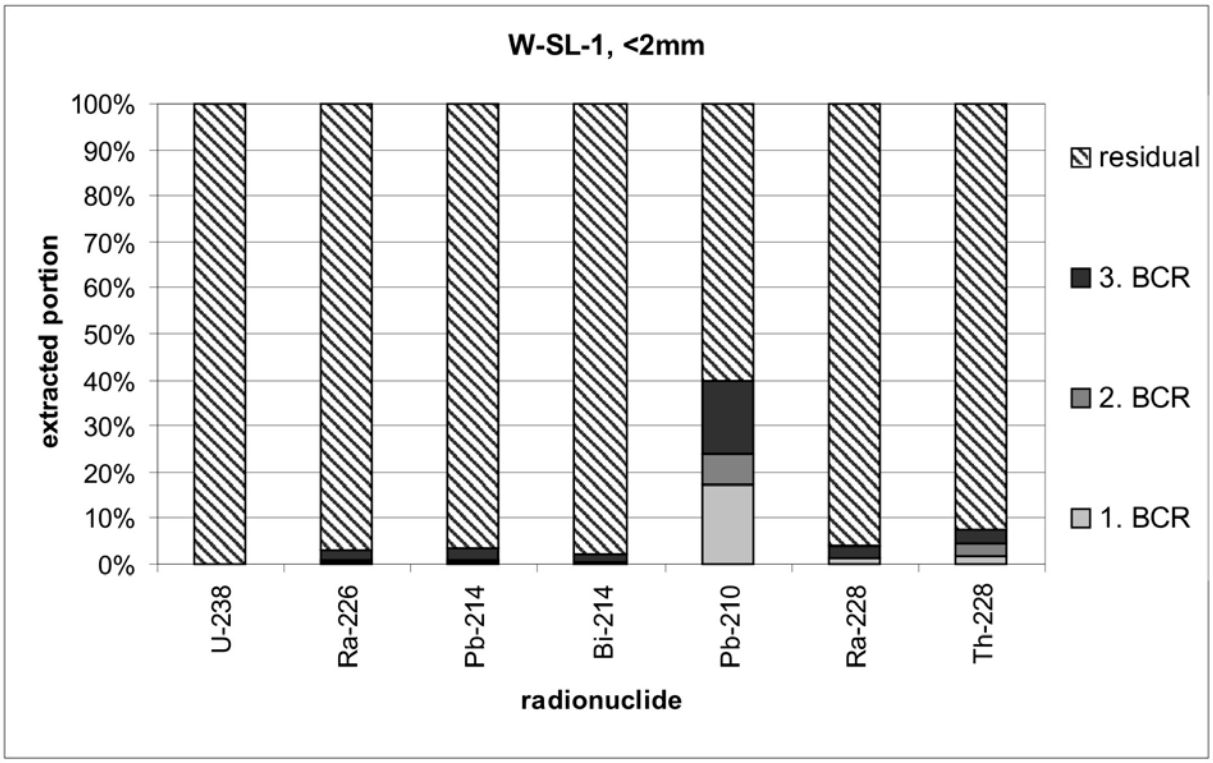

Fig. 5-47: Radionuclide fractions dissolved by BCR-procedure from the sludge W-SL-1, <2mm.

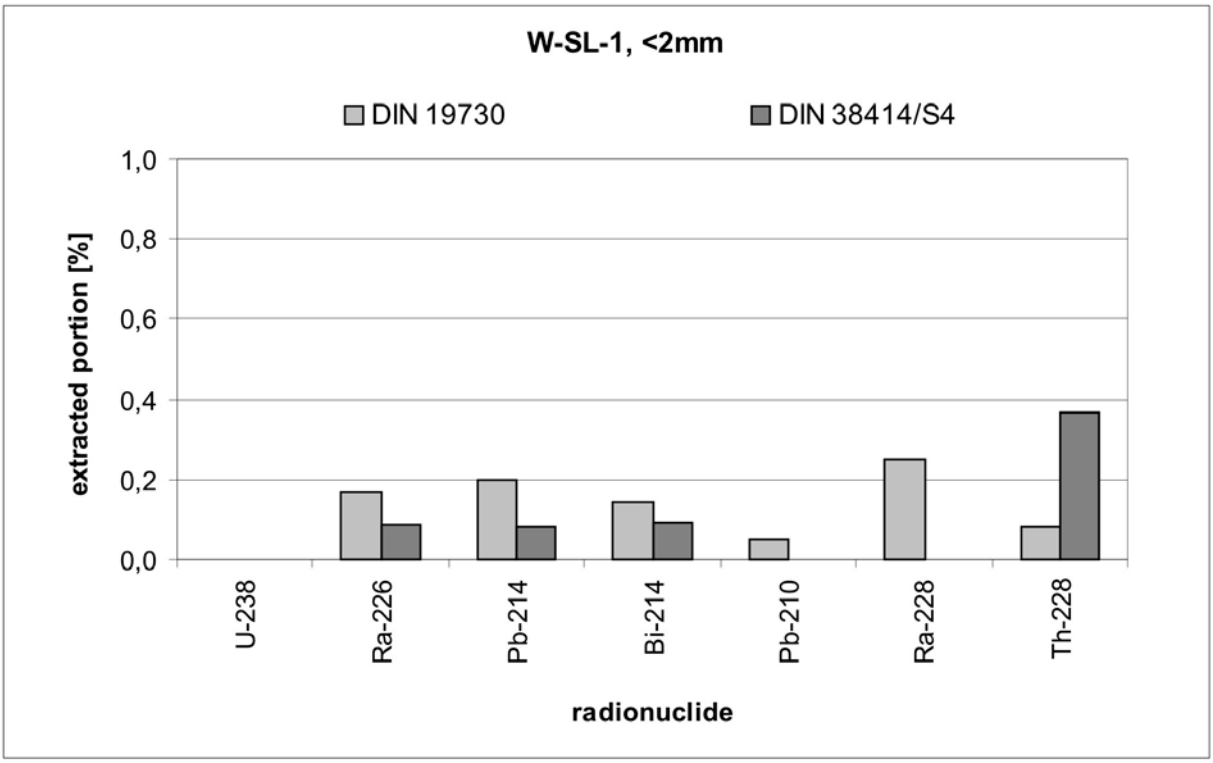

Fig. 5-48: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the sludge W-SL-1, <2mm.

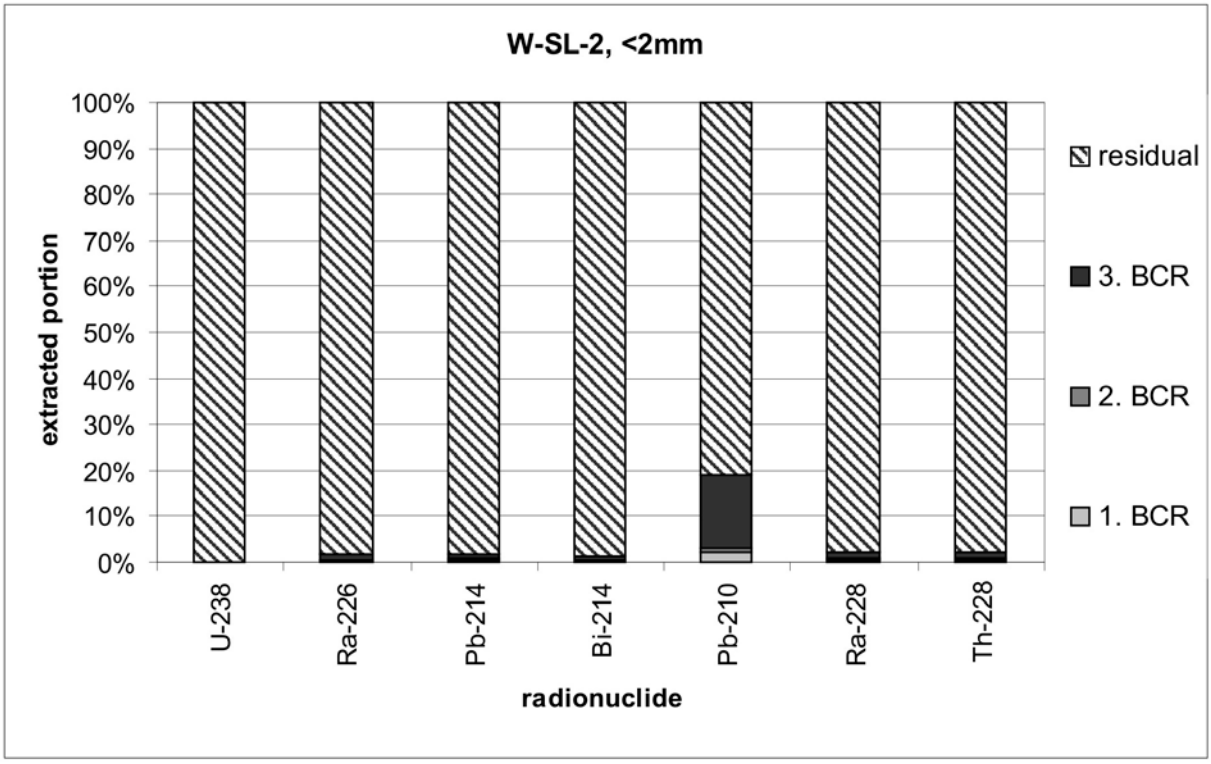

Fig. 5-49: Radionuclide fractions dissolved by BCR-procedure from the sludge W-SL-2, <2mm.

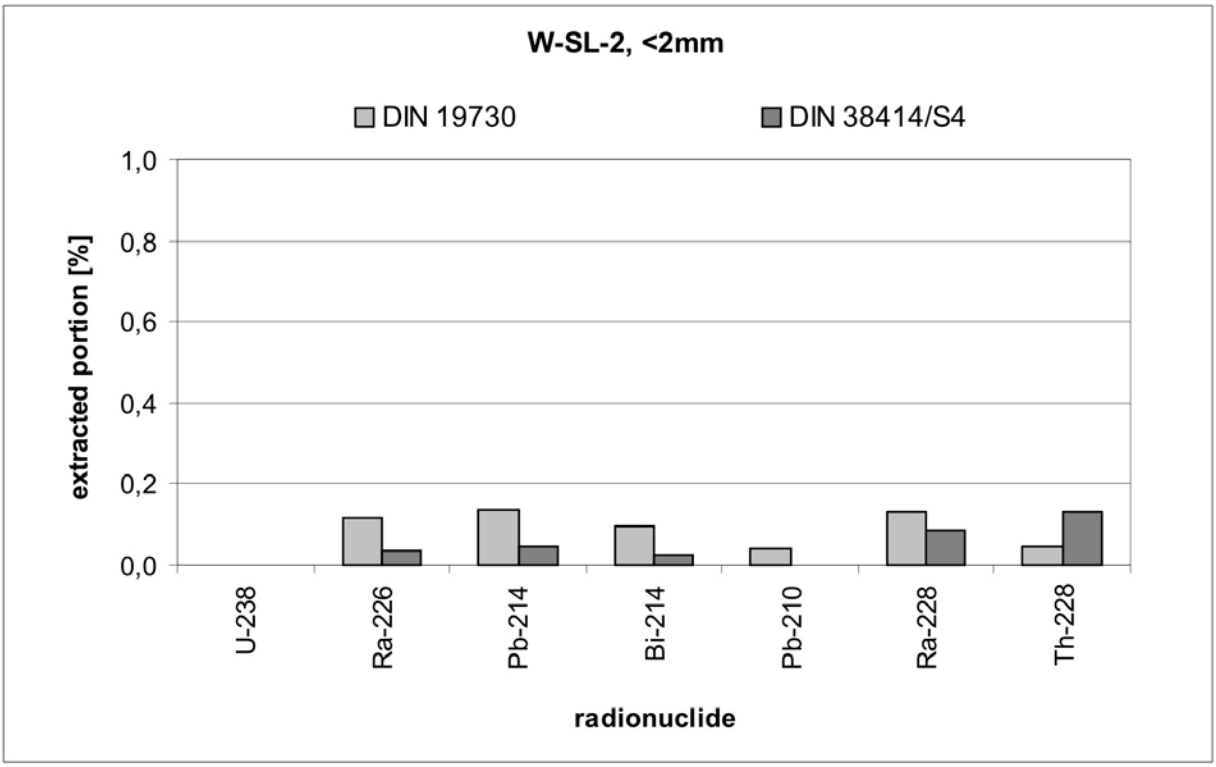

Fig. 5-50: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the sludge W-SL-2, <2mm.

organic matter and sulphides, 60% are left in the residual. 1% of ^{226}Ra can be found in the reducible respectively 2% in the oxidisable fraction, which is in well accordance with ^{228}Ra: 1% in 1. BCR and 2% in 3. BCR. ^{228}Th behaves similarly, 1% was detected in the easily exchangeable, 2% are bound to iron and manganese oxides and 3% are bound to organic matter and sulphides.

The plant available and water soluble fractions can be neglected, because all the measured radionuclides show a mobilisation potential lower than 0.4% (fig. 5-48). The second sludge sample W-SL-2, <2mm, shows radionuclides' leaching behaviours comparable with that first one. The radionuclide dissoluted in biggest volumes is ^{210}Pb by 19% in total (2% in 1. BCR, 1% in 2. BCR and 16% in 3. BCR fraction) beside a very few ^{226}Ra, ^{228}Ra and ^{228}Th, 2% each was detected in the organic matter and sulphide fraction (fig. 5-49). Once again, the plant availability and water solubility are not of importance, the leaching factors are constantly lower than 0.2% (fig. 5-50).

The scale sample W-SC-1, <2mm, is characterised by a complete dissolution of ^{210}Pb in frame of the BCR extraction procedure, 67% are present in the easily exchangeable fraction, 7% in the reducible and 26% in the oxidisable fraction (fig. 5-51). ^{226}Ra is only proven in the oxidisable fraction by 9%, whereas ^{228}Ra is distributed among the easily exchangeable fraction by 4% and 6% in the oxidisable fraction. ^{228}Th is found by 4% in the 1. BCR, 2% in the 2. BCR and 6% in the 3. BCR extract. The plant availability and water solubility can be neglected for all radionuclides due to really small leaching coefficients of lower than 0.8% (fig. 5-52). The ratios of all the radionuclides' extraction fractions measured from the second scale sample W-SC-2, <2mm, are comparable with the first one. It also shows the biggest BCR leaching volume for ^{210}Pb, in total by 31% (fig. 5-53). The most is present in the easily exchangeable (12%) and oxidisable (15%) fraction, only 4% were determined for the reducible fraction. ^{226}Ra is bound to manganese and iron oxides in a dimension of 2% and to organic matter and sulphides by 7%, ^{228}Ra only to organic matter and sulphides by 7%. ^{228}Th is fixed in the 1. BCR fraction by 4%, in the 2. BCR by 4% and in the 3. BCR by 6%. As described for W-SC-1, <2mm, the plant availability and water solubility do not affect one of the relevant radionuclides mentionable (fig. 5-54).

In summary, it can be stated that all the four samples resulting from crude oil exploitation provide ^{210}Pb especially by the easily exchangeable fraction and being bound to organic matter and sulphides in dimensions, which can not be denied. All the other radionuclides are not worth mentioning as well as their plant availability and water solubility.

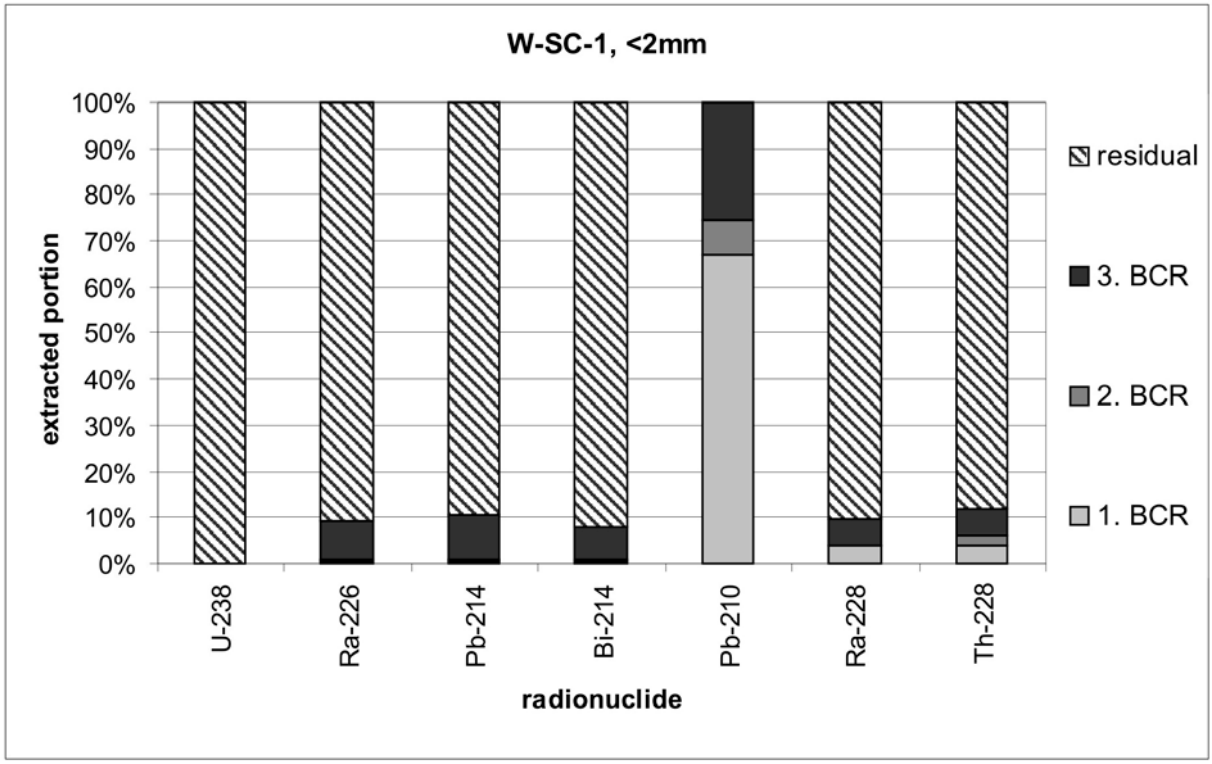

Fig. 5-51: Radionuclide fractions dissolved by BCR-procedure from the scale W-SC-1, <2mm.

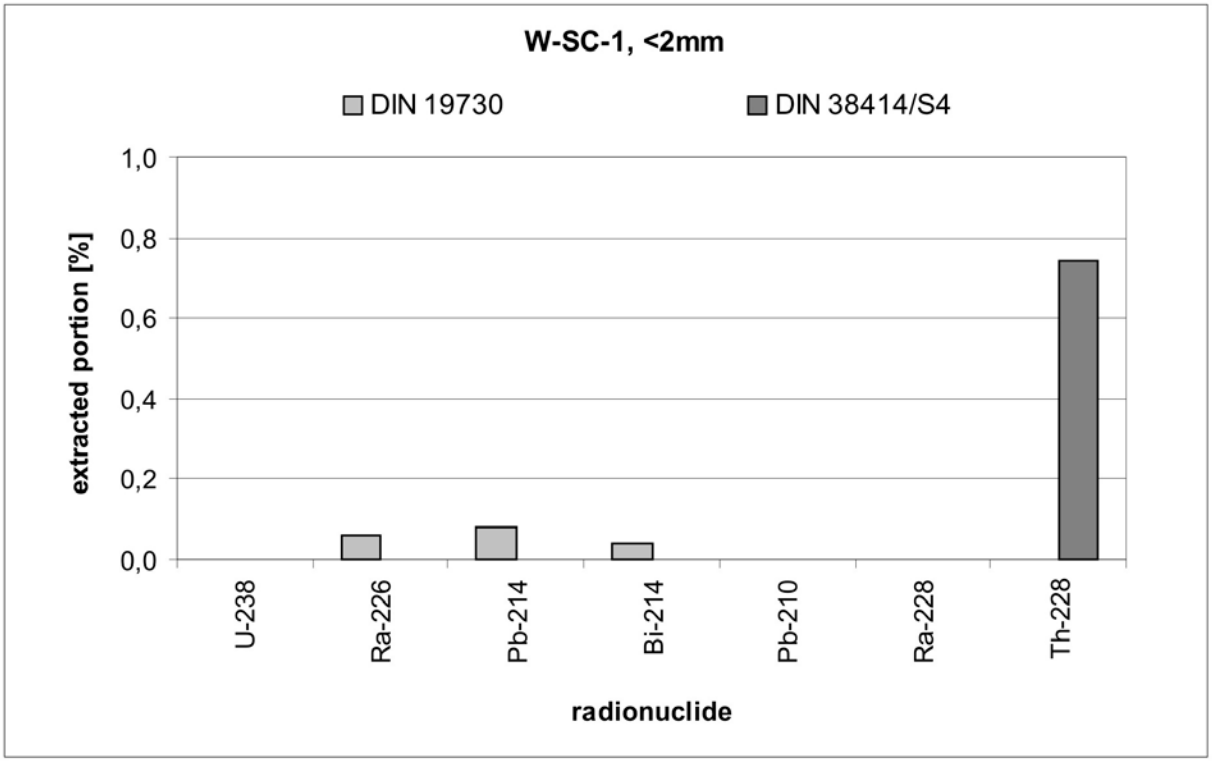

Fig. 5-52: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the scale W-SC-1, <2mm.

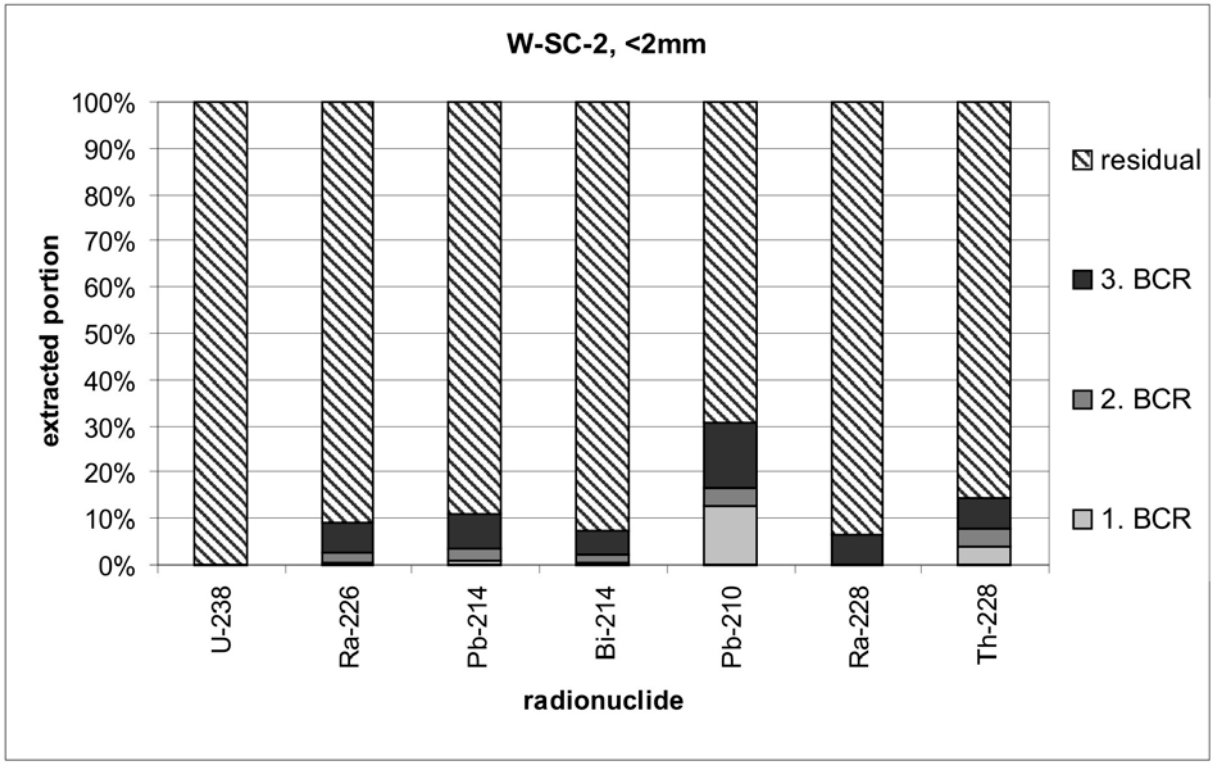

Fig. 5-53: Radionuclide fractions dissolved by BCR-procedure from the scale W-SC-2, <2mm.

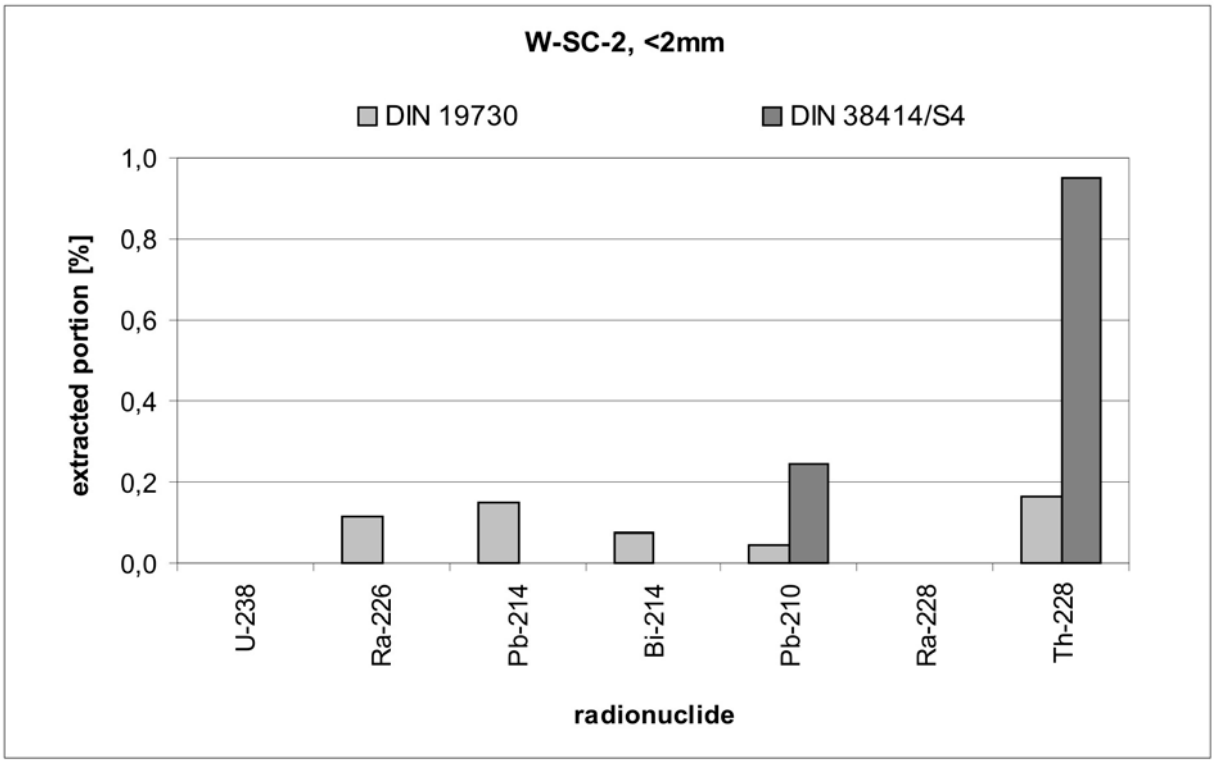

Fig. 5-54: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the scale W-SC-2, <2mm.

5.2.5 Hard coal extraction

Unfortunately, the four unwanted by-products from hard coal mining occurring as sediments along rivers were available in volumes, which just enable the BCR extraction procedure to have been carried out. But as obvious from the fig. 5-55, 5-56, 5-57 and 5-58, the

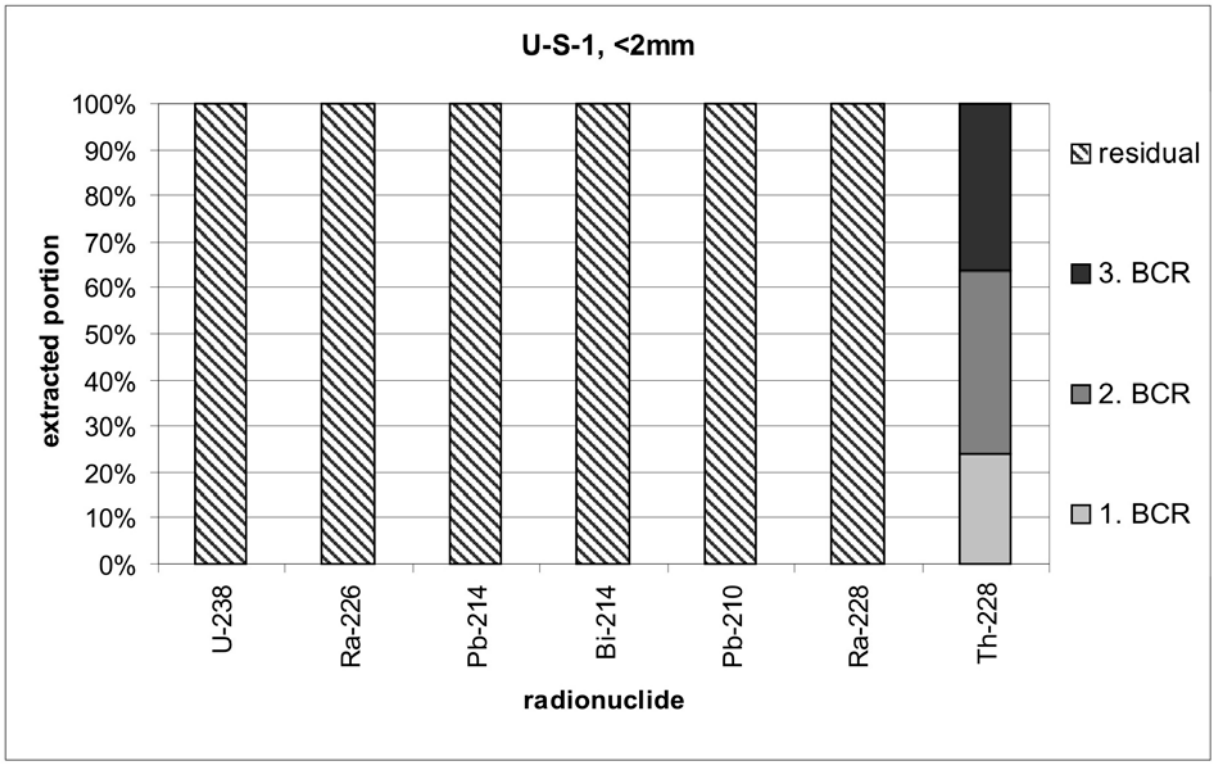

Fig. 5-55: Radionuclide fractions dissolved by BCR-procedure from the sediment U-S-1, <2mm.

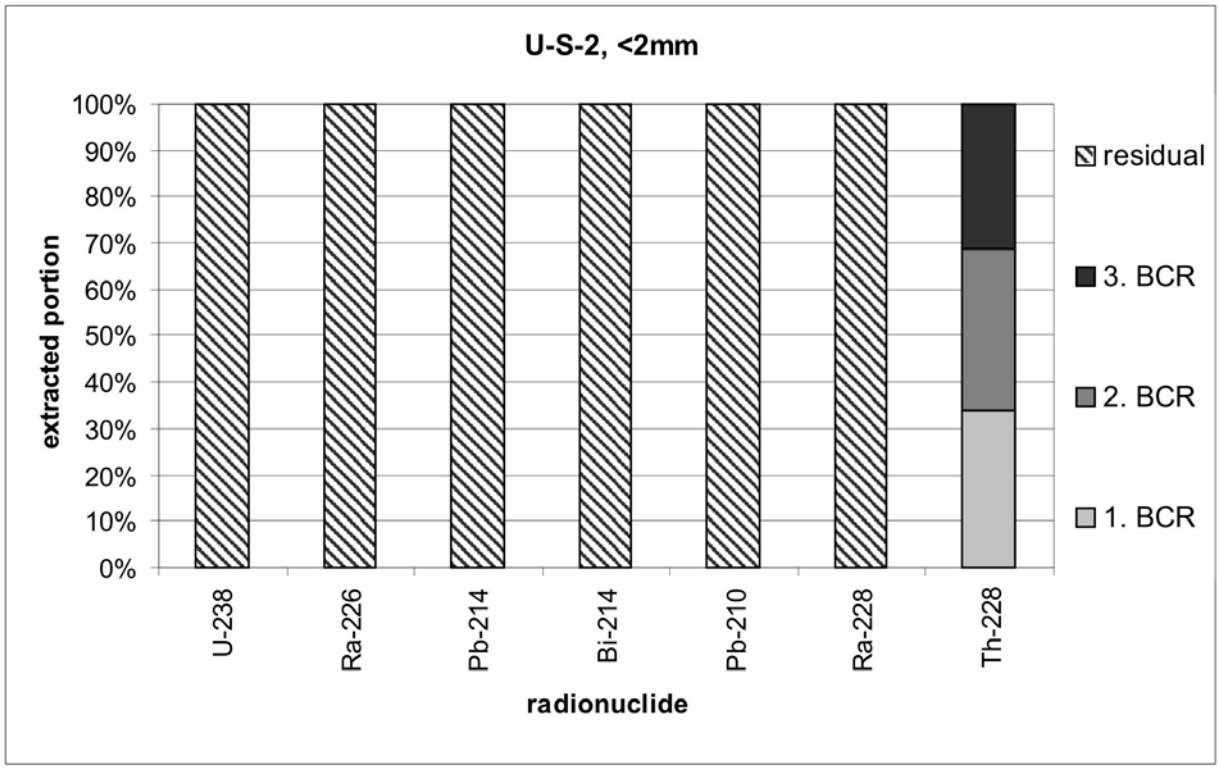

Fig. 5-56: Radionuclide fractions dissolved by BCR-procedure from the sediment U-S-2, <2mm.

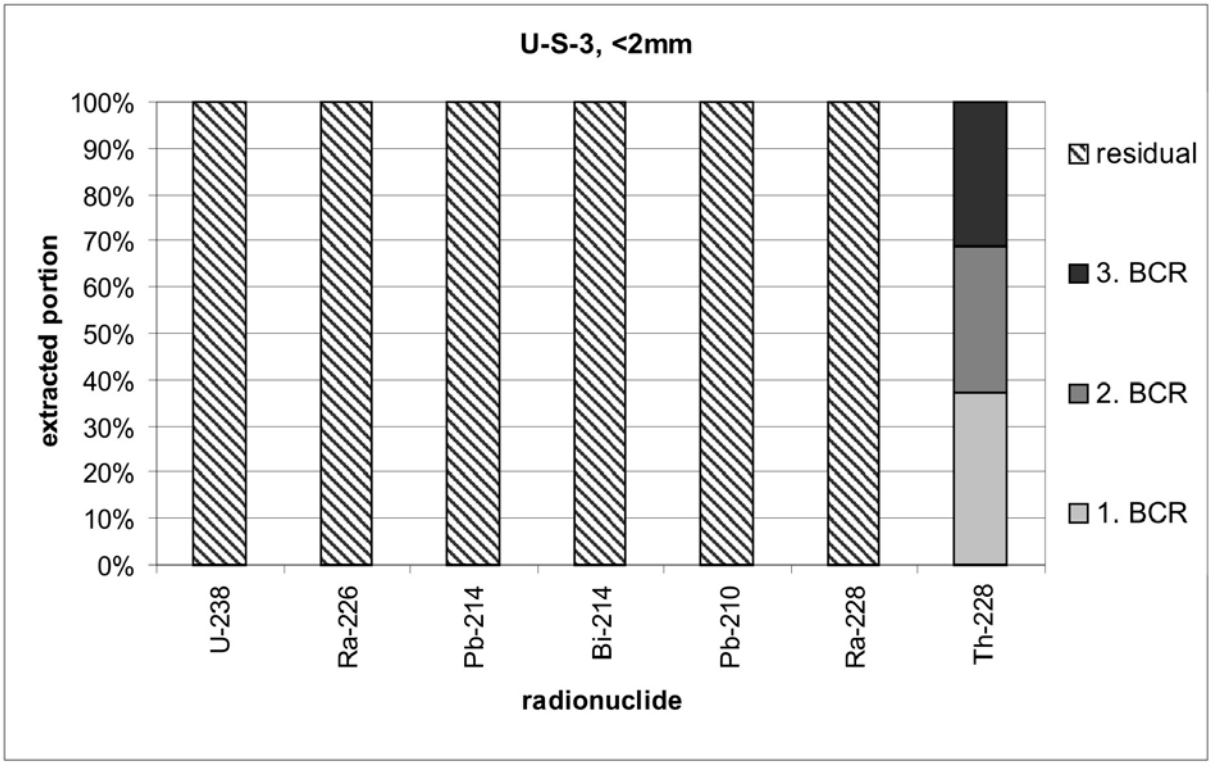

Fig. 5-57: Radionuclide fractions dissolved by BCR-procedure from the sediment U-S-3, <2mm.

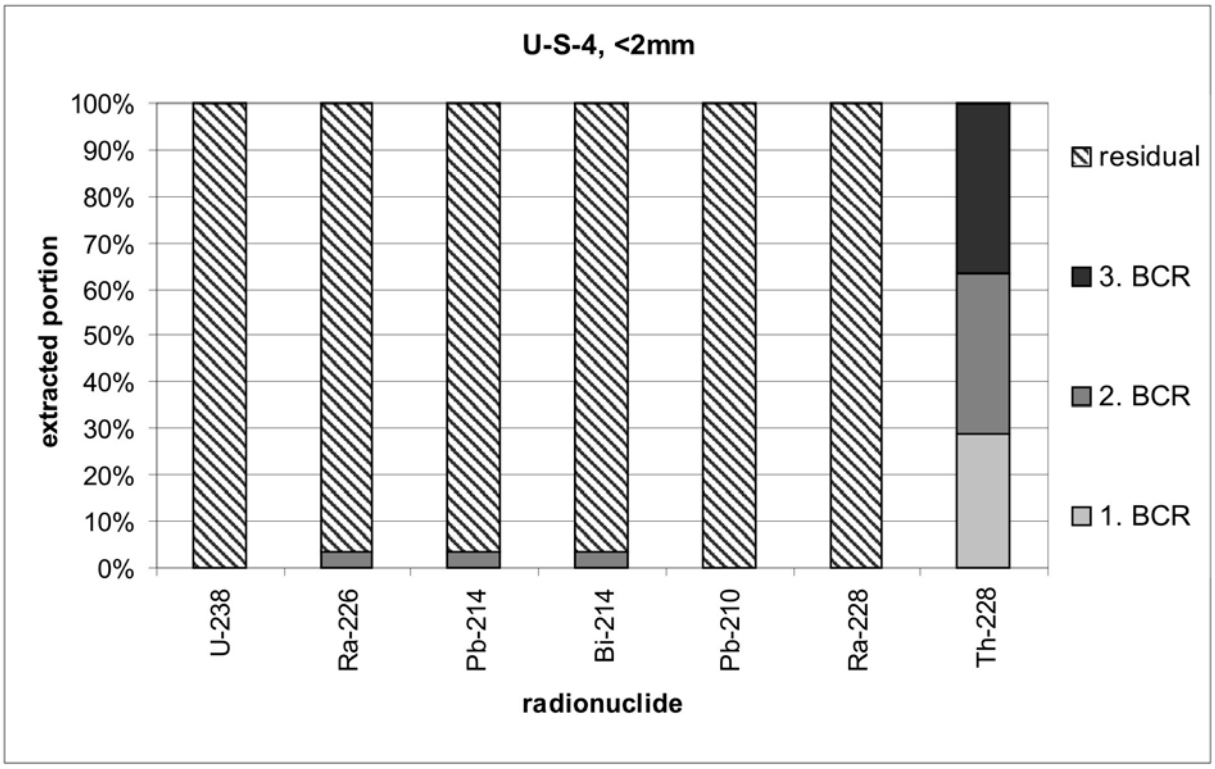

Fig. 5-58: Radionuclide fractions dissolved by BCR-procedure from the sediment U-S-4, <2mm.

radionuclides' leaching behaviour coincidents very well in all the four samples. The only leached radionuclide is ^{228}Th, which always occurs by similar ratios in the three BCR extraction fractions, each of roughly 33%. The other relevant radionuclides are not proven in any of the extraction liquids with the exemption of ^{226}Ra in sample U-S-4, <2mm, but the small portion of 3% being bound to iron and manganese oxides does not interrupt the general impression.

The sediment samples being affected by pit waters from hard coal mining do not provide any relevant radionuclide in mentionable amounts, the leached ^{228}Th portions get put into perspective by keeping in mind the very poor initial activity concentrations of less than 200Bq/kg (see chapter "5.1.5 Hard coal extraction"). The relative position of the sampling point, i.e. slip-off or undercut slope close to waterline or irregularly affected by flooding events, does not influence the radionuclides' type of bounding.

5.2.6 Thorium compounds industry

The thorium containing soil samples are delivered from two different sites: U-SO-1, <2mm, comes from the area being contaminated by residues of a former thorium catalyst, the other three soils are affected by thorium bearing dust. U-SO-1, <2mm, shows that ^{238}U and ^{226}Ra are only bound to iron and manganese oxides in dimensions of 8% respectively 6% (fig. 5-59), ^{228}Ra and ^{228}Th are present in all BCR fractions in similar ratios: ^{228}Ra was leached by 2% in the easily exchangeable fraction, 3% in the reducible and 7% in the oxidisable fraction, ^{228}Th by 1% in the 1. BCR, 2% in the 2. BCR and 7% in the 3. BCR fraction. ^{210}Pb was not measured in the initial material. Plant availability and water solubility are not of importance, ^{226}Ra was determined by 0.7%, ^{228}Ra by 1% and ^{228}Th by less than 0.1% to be plant available and no radionuclide was proven in the water soluble extraction liquids (fig. 5-60).

A different picture is given by the dust contaminated soils. In all cases, ^{226}Ra was completely dissolved in frame of the BCR extraction procedure, but in varying ratios. U-SO-2, <2mm, and U-SO-3, <2mm, are well comparable in their characteristics to provide radionuclides. U-SO-2, <2mm, leads to ^{226}Ra of 17% in the easily exchangeable fraction, 46% are bound to iron and manganese oxides and 37% to organic matter and sulphides (fig. 5-61). ^{210}Pb is fixed in the easily exchangeable fraction by 9% and in the reducible one by 13%. The important ^{232}Th progenies are present as follows: ^{228}Ra by 19% in the 1. BCR, 23% 2. BCR and 23% in the 3. BCR fraction, ^{228}Th by 11% in the 1. BCR, 14% in the 2. BCR and 25% in the 3. BCR fraction. A similar picture is given for U-SO-3, <2mm, which provides ^{226}Ra by 9% for the easily exchangeable, 64% for the reducible and 27% for the oxidisable fraction (fig. 5-63). ^{210}Pb can be exclusively found by 23% in the oxidisable fraction. ^{228}Ra is bound in the easily exchangeable fraction by 18%, 33% are bound to iron and manganese oxides and 20% to organic matter and sulphides, the progeny ^{228}Th is proven by 10% in the easily exchangeable, 19% in the reducible and 23% in the oxidisable fraction. Also the plant availability and water solubility are in well accordance, 1.5% of the inital ^{238}U, 0.2% of ^{226}Ra, 1% of ^{210}Pb, 5.5% of ^{228}Ra and 0.7% of ^{228}Th are plant available from U-SO-2 (fig. 5-62), 3.8% of ^{238}U, 3% ^{226}Ra, no lead, 6.3% of ^{228}Ra and 0.4% of ^{228}Th from U-SO-3 (fig. 5-64). Water solubility can not be observed in both cases. The third sample U-SO-4, <2mm, behaves slightly different, its ^{226}Ra content is distributed among the 1. BCR fraction by 69%, the 2. BCR by 15% and the 3. BCR by 16% (fig. 5-65). ^{238}U and ^{228}Ra are not present in the soil and ^{210}Pb and ^{228}Th are left unsolved in the residual. 33% of ^{226}Ra are determined to be water soluble, 14% to be plant available (fig. 5-66). 52% of ^{228}Th is detected only in the water soluble fraction, whereas ^{238}U, ^{210}Pb and ^{228}Ra were not measured in any of both extractants.

In summary, it must be emphasised that despite its relatively low BCR leaching coefficients, sample U-SO-1 does contain the by far highest initial activity concentrations of more than 400,000Bq/kg for each of the ^{232}Th progenies, which also concerns the low ^{228}Ra water solubility of 1%. Especially both the soil samples U-SO-2 and U-SO-3 correspond very well in their

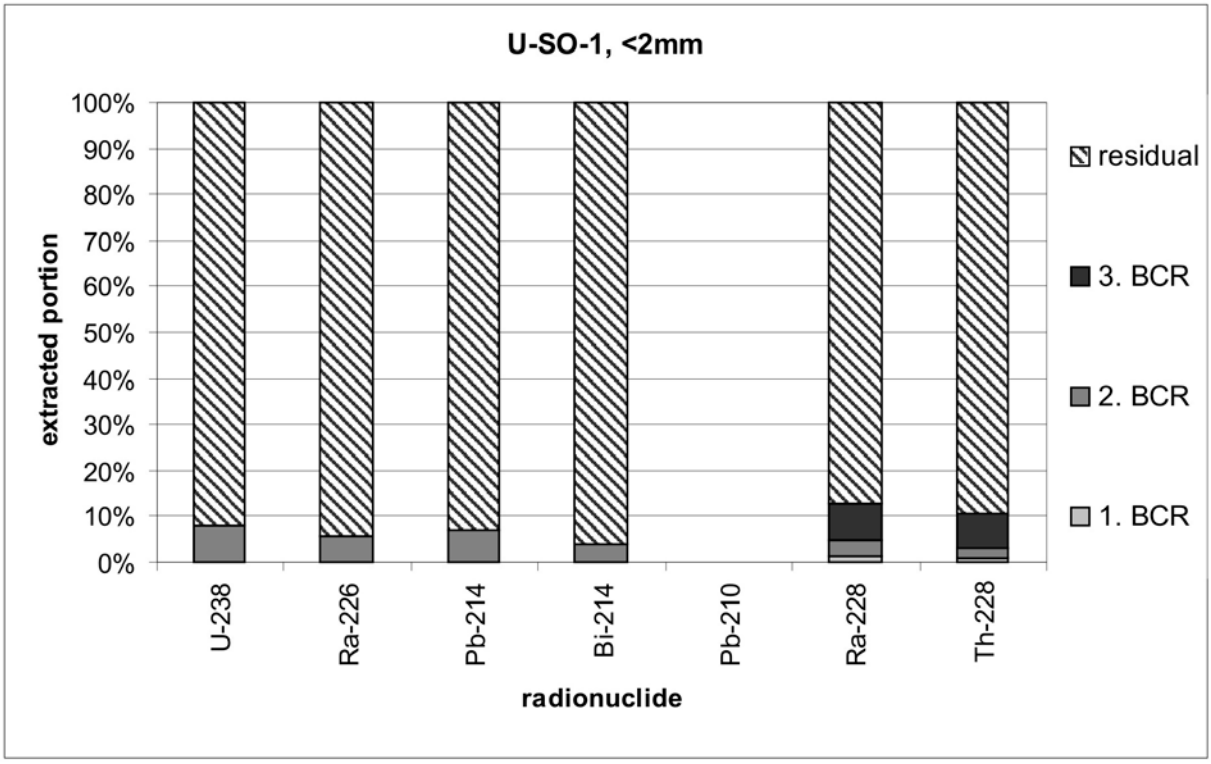

Fig. 5-59: Radionuclide fractions dissolved by BCR-procedure from the soil U-SO-1, <2mm.

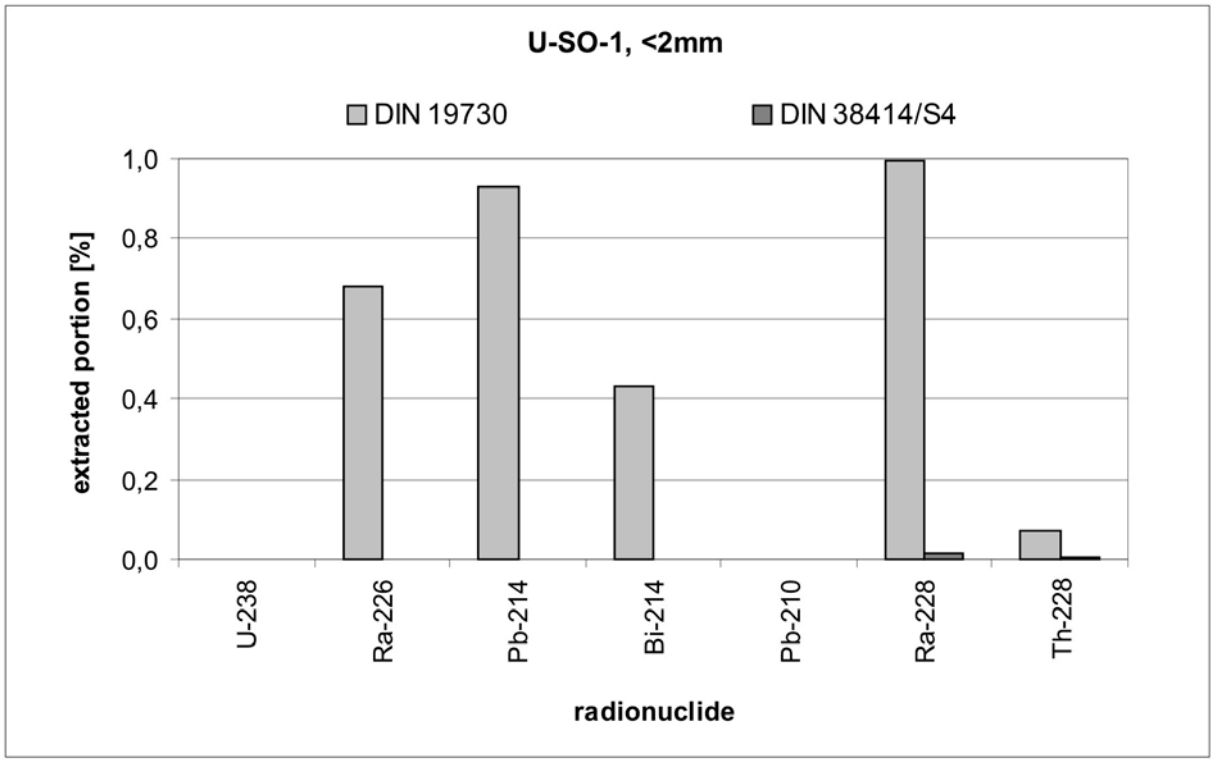

Fig. 5-60: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the soil U-SO-1, <2mm.

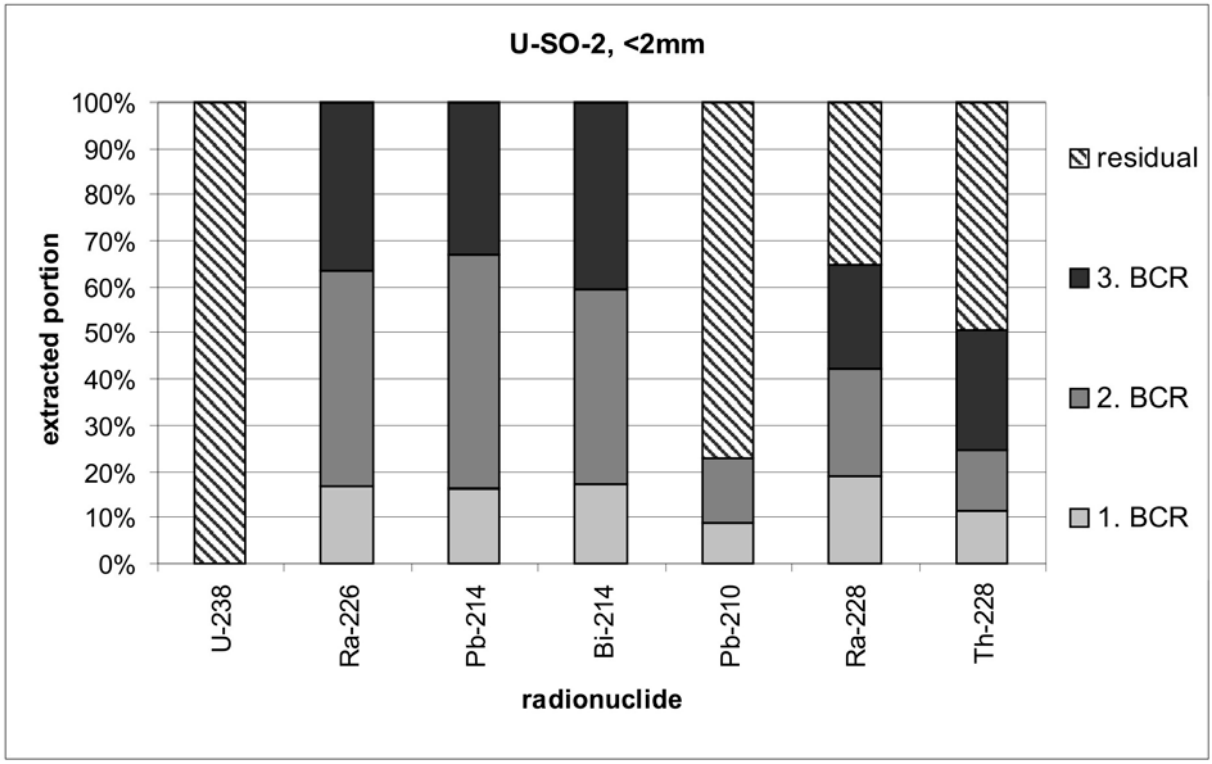

Fig. 5-61: Radionuclide fractions dissolved by BCR-procedure from the soil U-SO-2, <2mm.

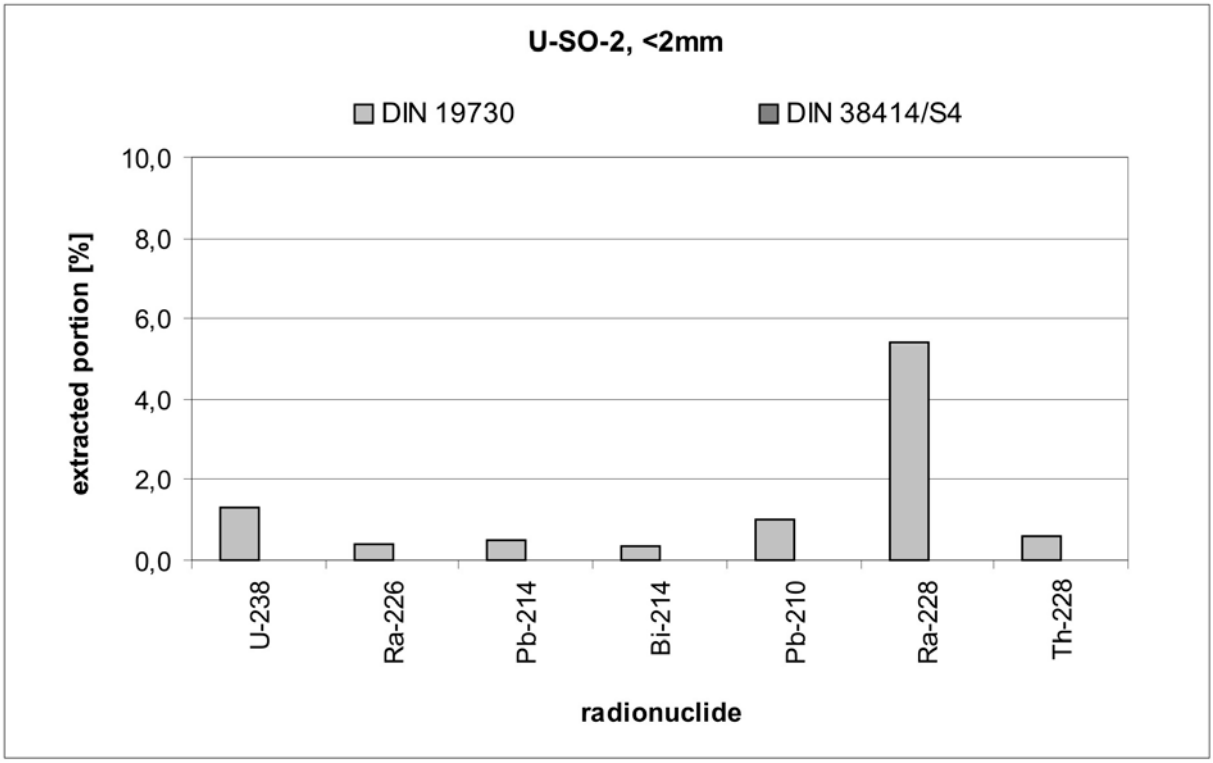

Fig. 5-62: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the soil U-SO-2, <2mm.

radionuclides' leaching behaviour in frame of all three extraction procedures. The determined extractable radionuclide amounts of U-SO-4 are of lower importance due to the small initial activity concentrations of continously less than 100Bq/kg.

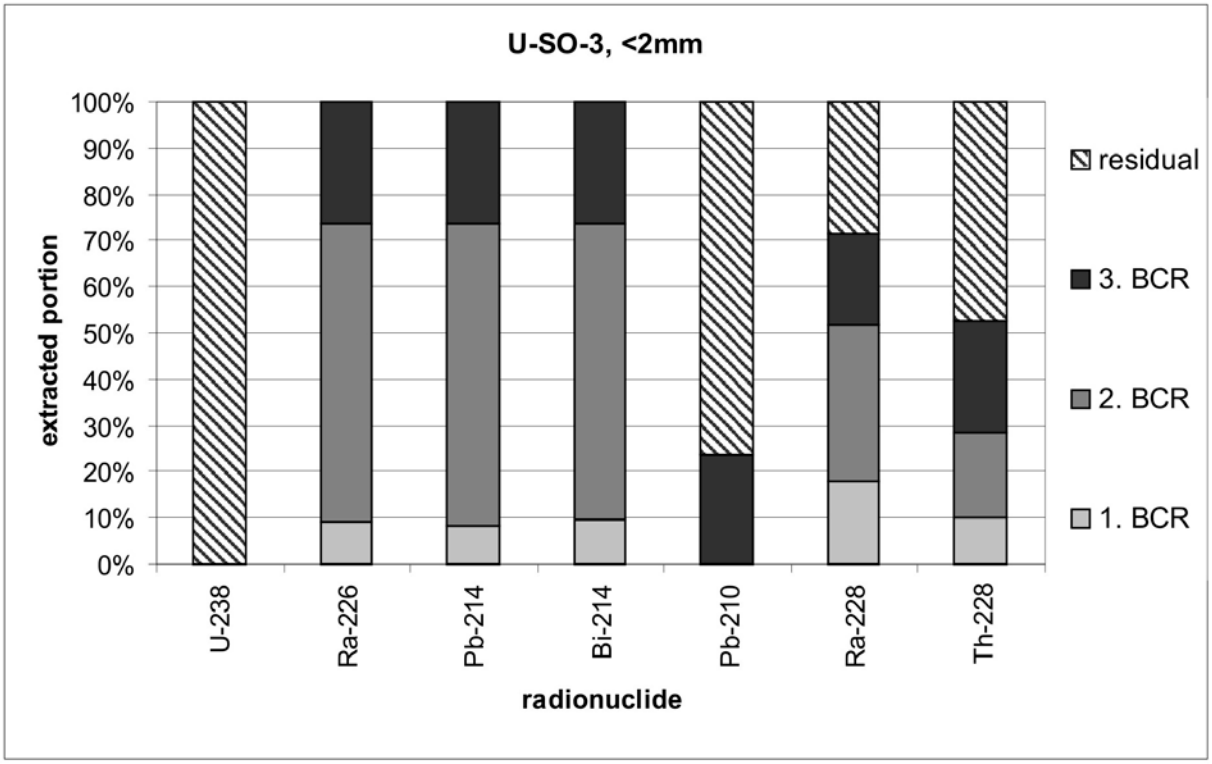

Fig. 5-63: Radionuclide fractions dissolved by BCR-procedure from the soil U-SO-3, <2mm.

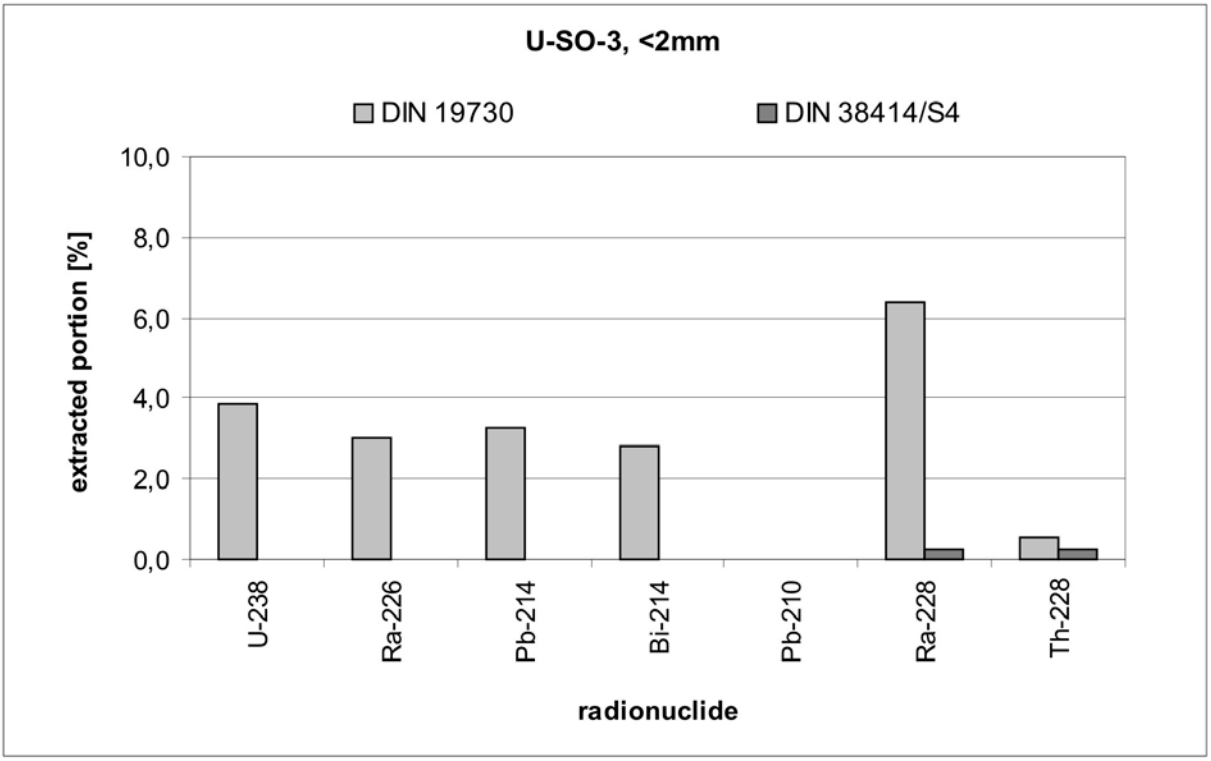

Fig. 5-64: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the soil U-SO-3, <2mm.

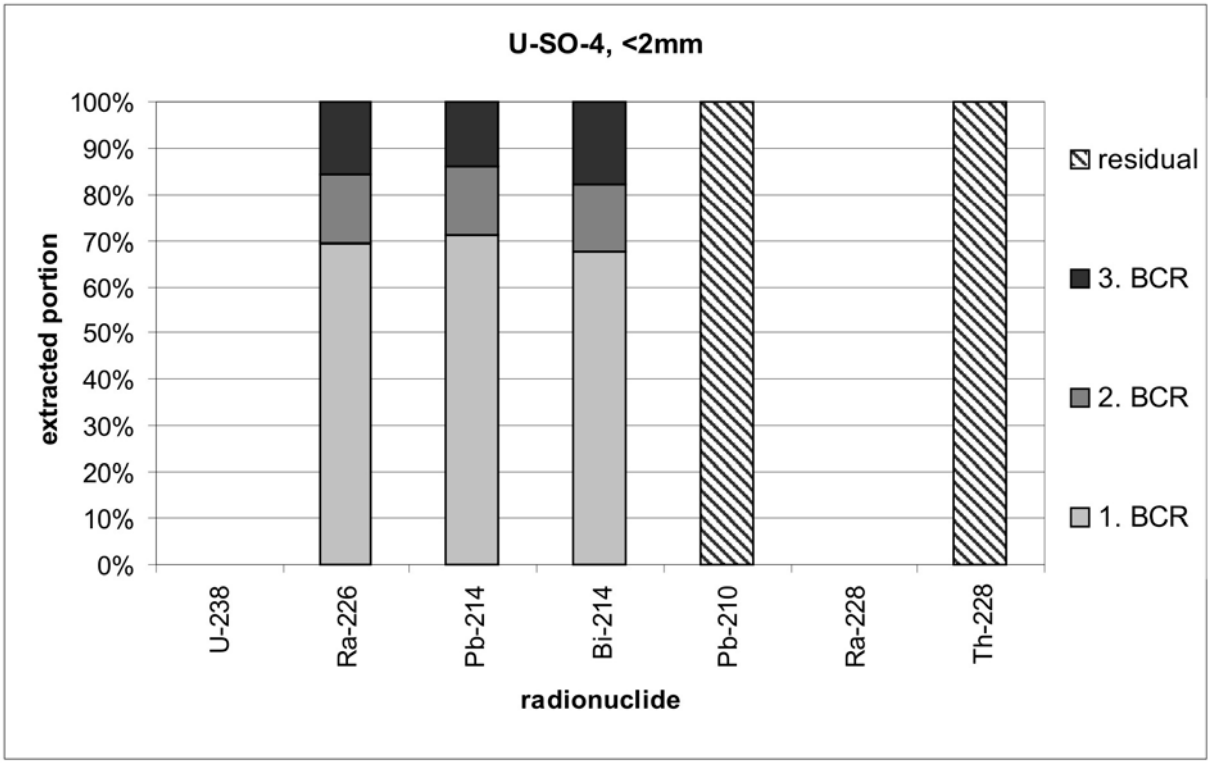

Fig. 5-65: Radionuclide fractions dissolved by BCR-procedure from the soil U-SO-4, <2mm.

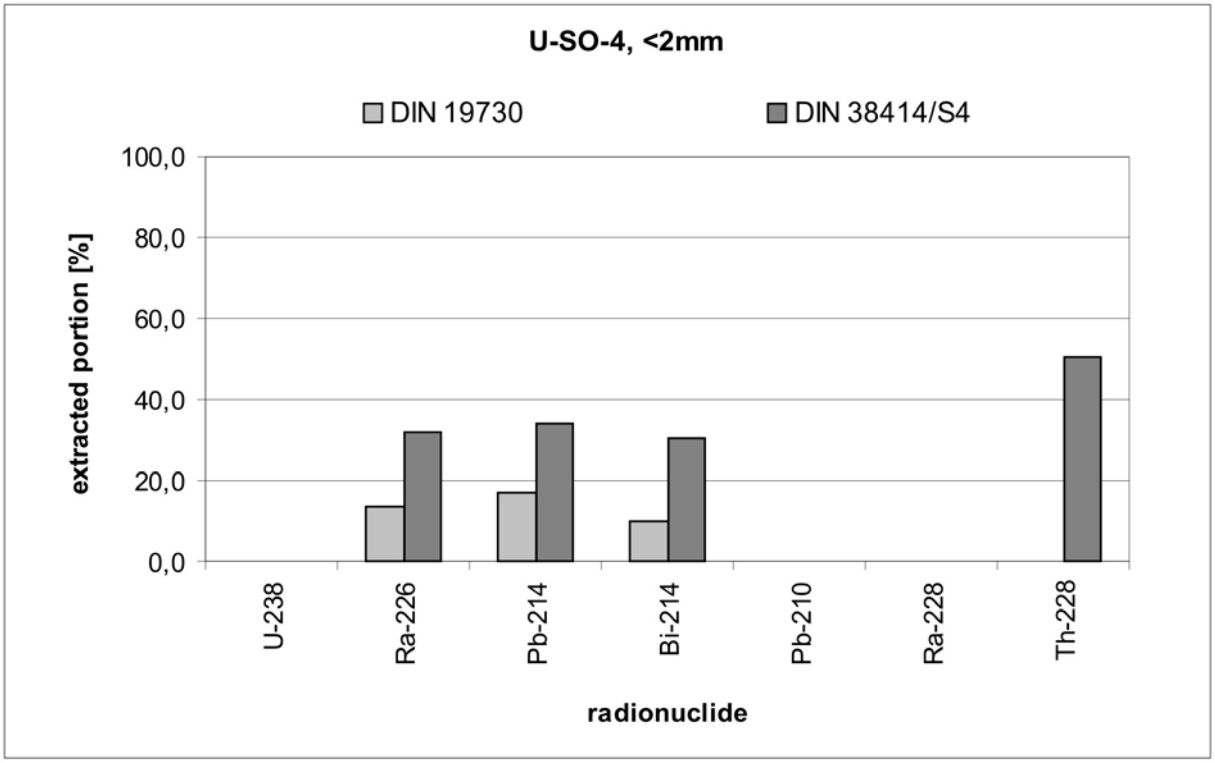

Fig. 5-66: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the soil U-SO-4, <2mm.

5.2.7 Uranium industry

Within this thesis, the most samples were collected from the uranium processing industry simply justified by the presence of those sites in two of the TENORMHARM participants' countries (Czech Republic and Slovenia).

The uranium bearing ores R-UO-1, <0.1mm, and R-UO-2, <0.1mm, were available in such small dimensions, which only allow the BCR extraction procedure to have been carried out, unfortunately. Since both have been taken as hard rocks, just the grain size <0.1mm were part of investigations being in accordance with the developed sample treatment scheme (see chapter "4. Material preparation and examination methods"). On the one hand, both samples were not proven to contain any progeny of the ^{232}Th decay series, but on the other they are characterised by pretty different types of bounding concerning the uranium decay series' radionuclides. Sample R-UO-1 shows a similar leaching behaviour for all those elements (fig. 5-67), whereas from R-UO-2 ^{238}U and ^{210}Pb are almost completely leached in frame of the BCR extraction procedure whilst ^{226}Ra turns out of interest (fig. 5-68). The ratios for the radionuclides of R-UO-1 being distributed among the three BCR extraction fractions are as follows (fig. 5-67):

^{238}U:	27% 1. BCR,	6% 2. BCR,	15% 3. BCR fraction
^{226}Ra:	10% 1. BCR,	21% 2. BCR,	16% 3. BCR fraction
^{210}Pb:	11% 1. BCR,	11% 2. BCR,	11% 3. BCR fraction

In contrast, the initial ^{238}U content of R-UO-2 was completely leached during the BCR procedure, spread by a third among all three extraction steps (1. BCR: 36%, 2. BCR: 33%, 3. BCR: 31%) (fig. 5-68). ^{226}Ra is absolutely rarely dissolved and bound to iron and manganese oxides and organic matter and sulphides by 1% each, but lead is present in the easily exchangeable fraction by 8%, in the reducible by 43% and in the oxidisable fraction by 32%.

The slag samples U-ST-1, <0.1mm, and U-ST-2, <0.1mm, from stockpiles show comparable leaching behaviours for all relevant readionuclides. In both cases, from the uranium decay series only ^{238}U was leached by the BCR procedure and is present in the reducible fraction in large portions (U-ST-1: 56% beside 44% in the easily exchangeable fraction (fig. 5-69); U-ST-2: 100%, (fig. 5-71)). ^{228}Th is fixed in the three BCR fractions roughly by a third, in U-ST-2 ^{228}Ra occurs additionally (fig. 5-71). ^{226}Ra and ^{210}Pb were not detected in any of those extraction liquids. 85% of the initial ^{238}U content, 55% of ^{226}Ra, 62% of ^{228}Ra and 47% of ^{228}Th are determined to be water soluble from U-ST-1, plants might be affected by 13% ^{238}U and 14% ^{228}Th (fig. 5-70). U-ST-2 provides 77% of ^{238}U and 63% of ^{228}Th for water solubility, 15% of the latter are also plant available (fig. 5-72).

The other hard rocks from stockpiles are the pegmatite U-ST-3, <0.1mm, and the uranium bearing breccia U-ST-4, <0.1mm, and both coincident in their mobilisation potentials for natural radionuclides. The pegmatite contains ^{238}U by 18% in the easily exchangeable and by 82% in the oxidisable fraction, ^{226}Ra is present in the 1. BCR by 4%, in the 2. BCR by 7% and in the 3. BCR fraction by 29% whereas ^{210}Pb is exclusively bound to organic matter and sulphides by 28% (fig. 5-73). ^{228}Th is distributed by a third roughly among all three BCR fractions. The breccia's

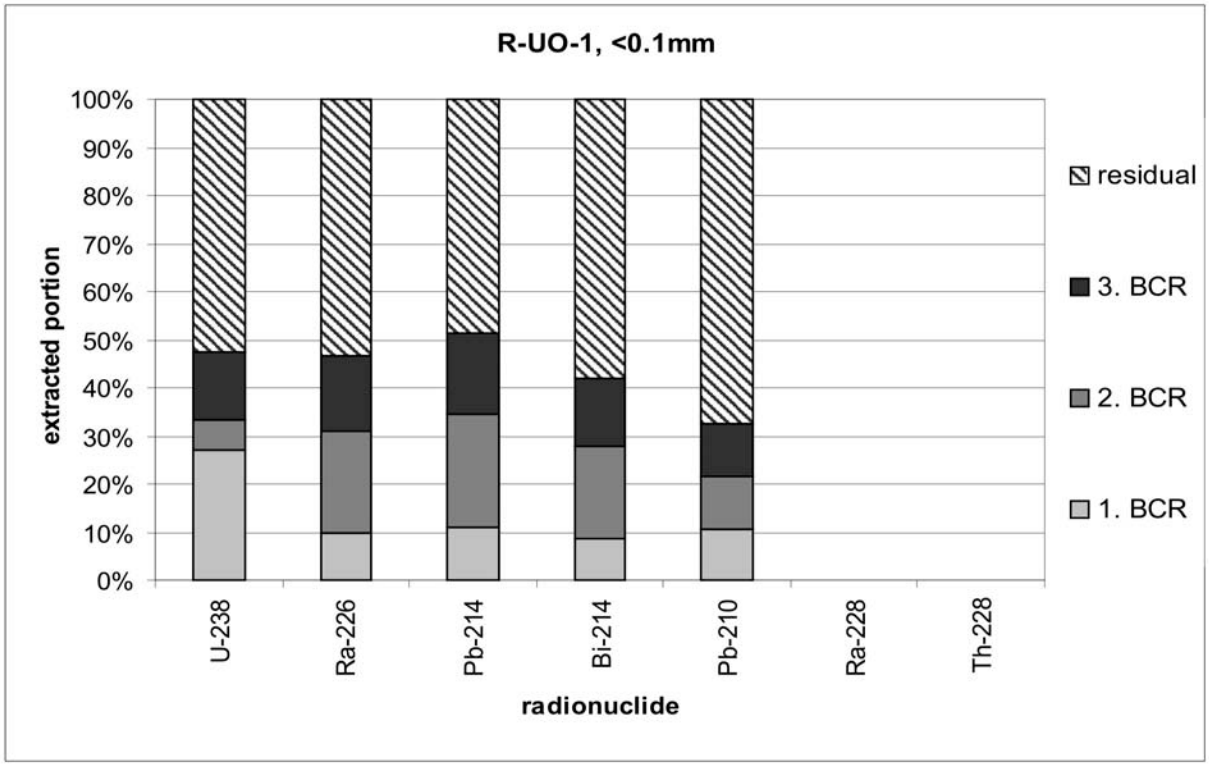

Fig. 5-67: Radionuclide fractions dissolved by BCR-procedure from the uranium ore R-UO-1, <0.1mm.

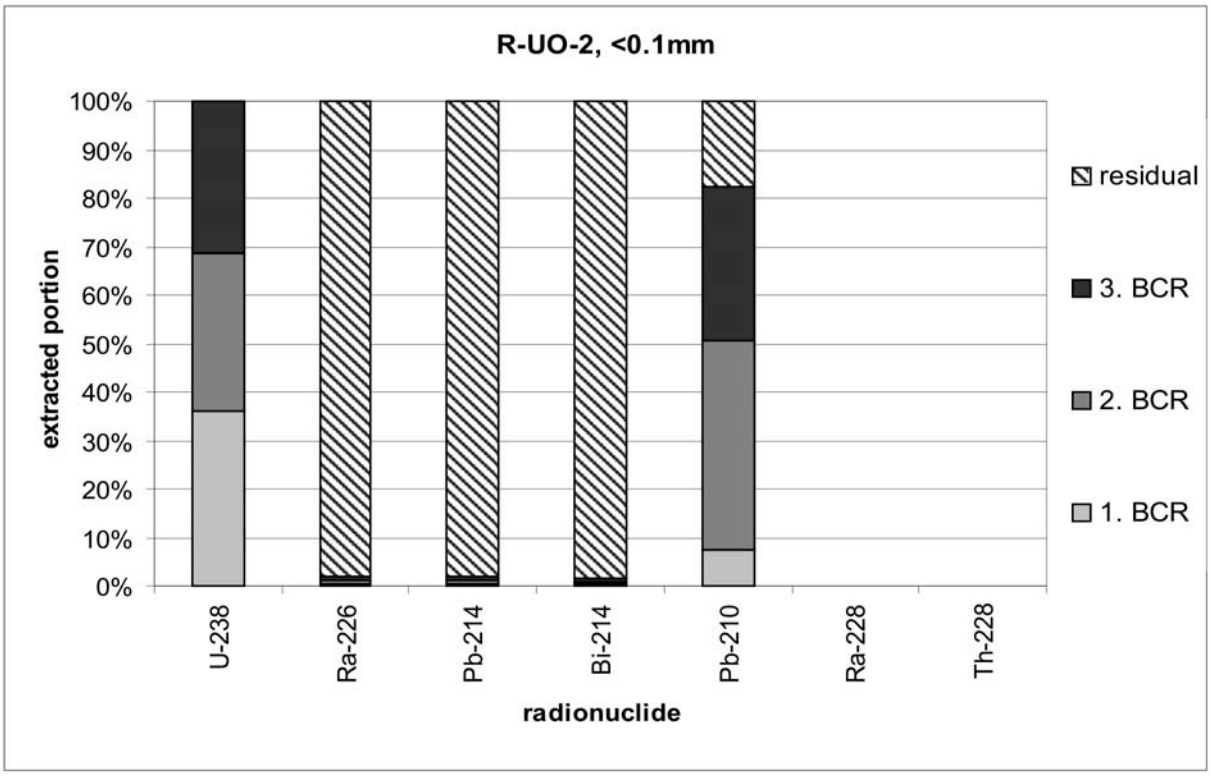

Fig. 5-68: Radionuclide fractions dissolved by BCR procedure from the uranium ore R-UO-2, <0.1mm.

^{238}U is fixed in the easily exchangeable fraction by 5%, 1% are due to iron and manganese oxides and 70% to organic matter and sulphides (fig. 5-75). ^{226}Ra is found by 1% as easily exchangeable, 3% to be reducible and 41% to be oxidisable, ^{210}Pb is almost completely bound to organic matter and sulphides by 84% beside 1% found in the 1. BCR fraction and 13% left in the residual.

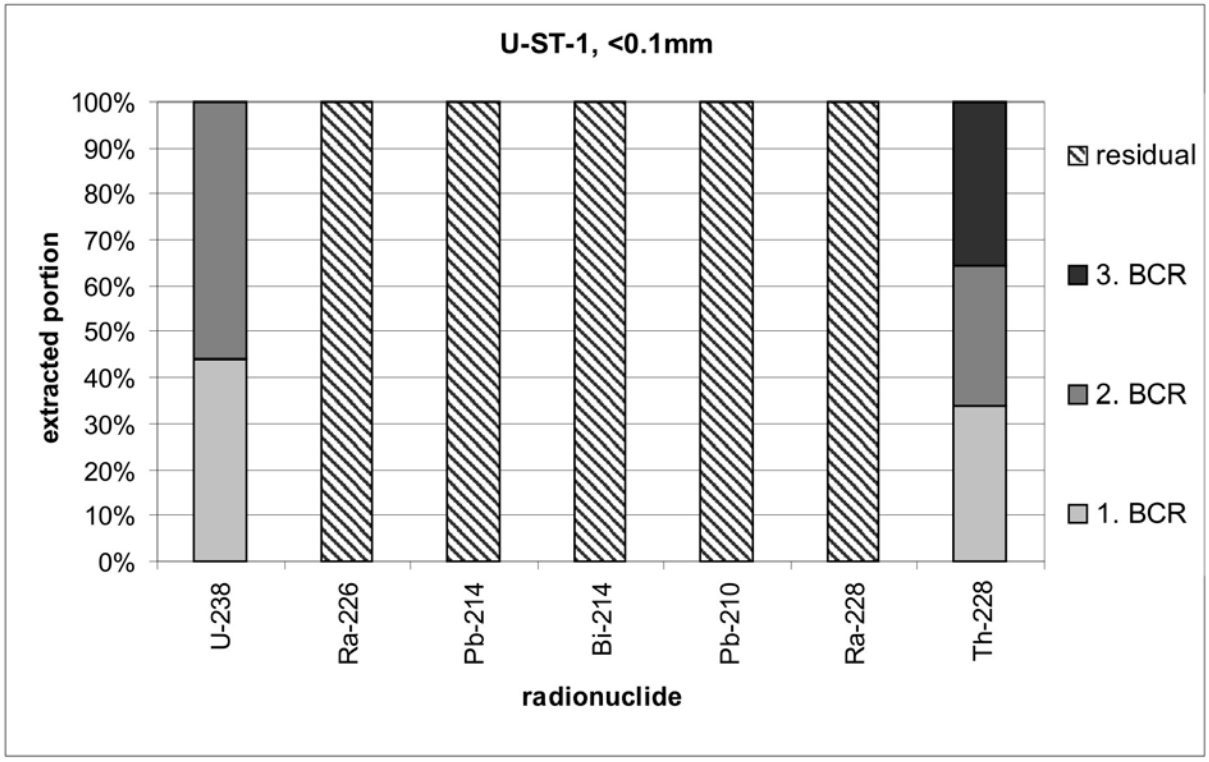

Fig. 5-69: Radionuclide fractions dissolved by BCR-procedure from the stockpile dead rock U-ST-1, <0.1mm.

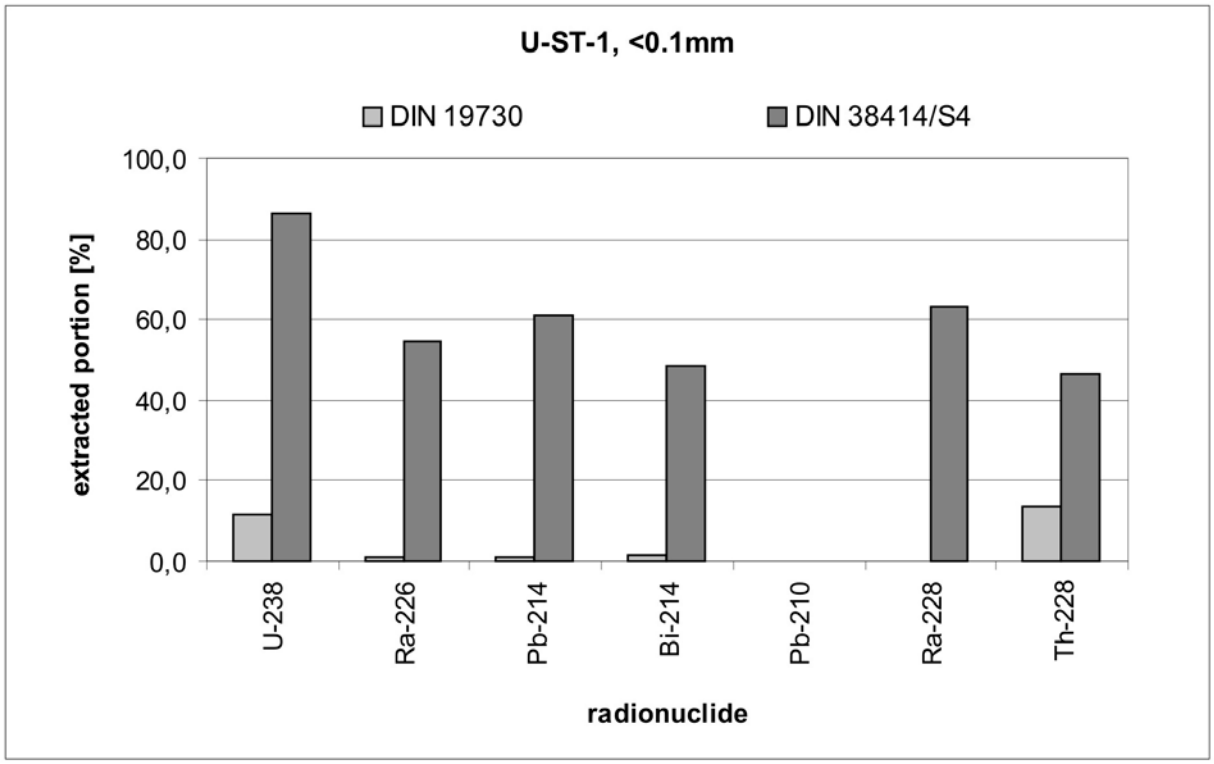

Fig. 5-70: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the stockpile dead rock U-ST-1, <0.1mm.

Despite ^{228}Th of U-ST-3, whose 100% leaching coefficient is put into perspective by its initial activity concentration of lower than 100Bq/kg, no radionuclide is proven to be water soluble from both samples (fig. 5-74 and 5-76). In contrast, 15% of the ^{238}U content and 14% of ^{226}Ra are determined to be available for plants from the pegmatite (fig. 5-74), the 66% factor of ^{228}Th turns

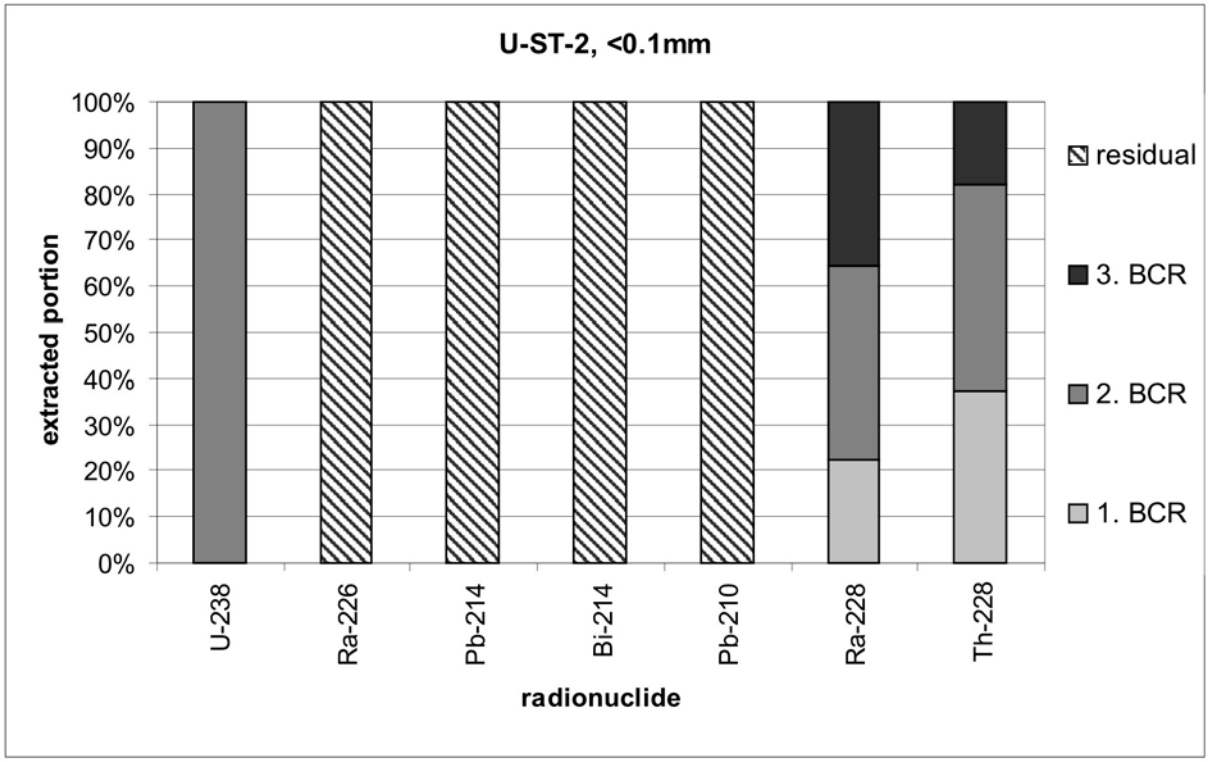

Fig. 5-71: Radionuclide fractions dissolved by BCR-procedure from the stockpile dead rock U-ST-2, <0.1mm.

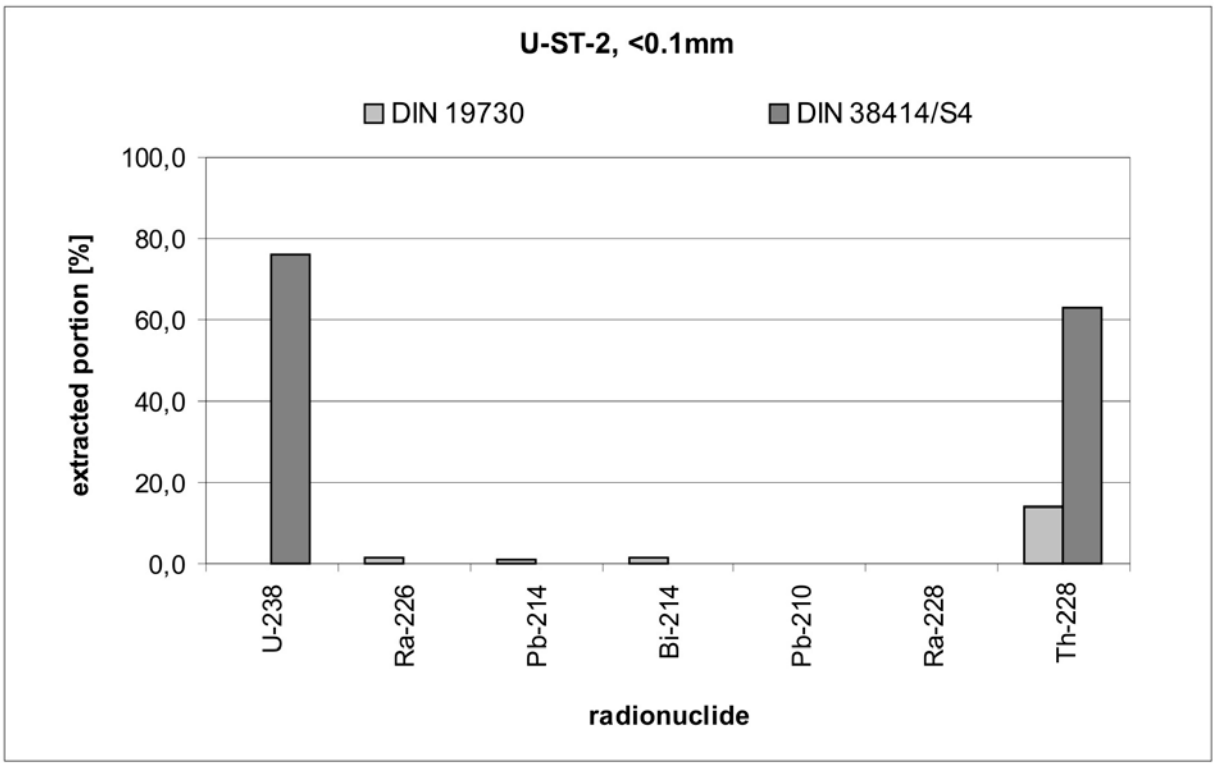

Fig. 5-72: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the stockpile dead rock U-ST-2, <0.1mm.

out of interest as mentioned before. The breccia provides only 6.3% of uranium and 4% of ^{226}Ra (fig. 5-76), but their initial activity concentrations were detected as ranging around 100,000Bq/kg (see chapter "5.1.7 Uranium industry").

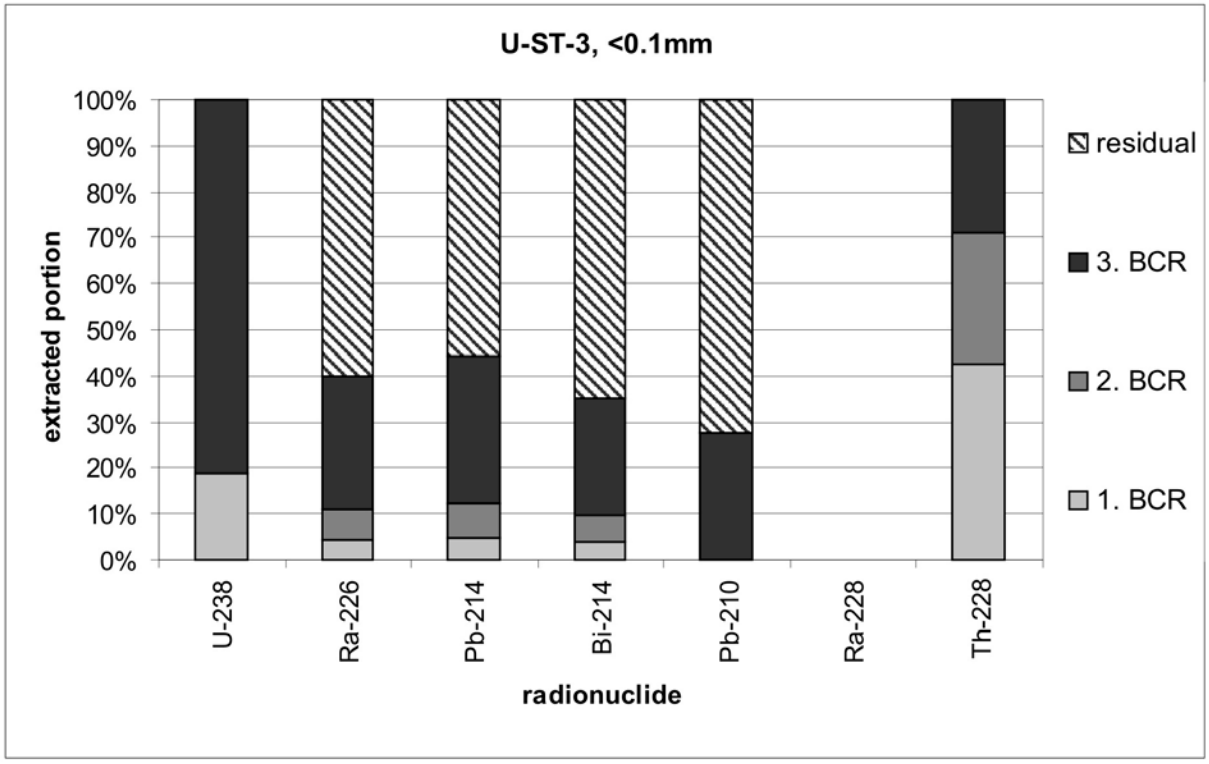

Fig. 5-73: Radionuclide fractions dissolved by BCR-procedure from the stockpile dead rock U-ST-3, <0.1mm.

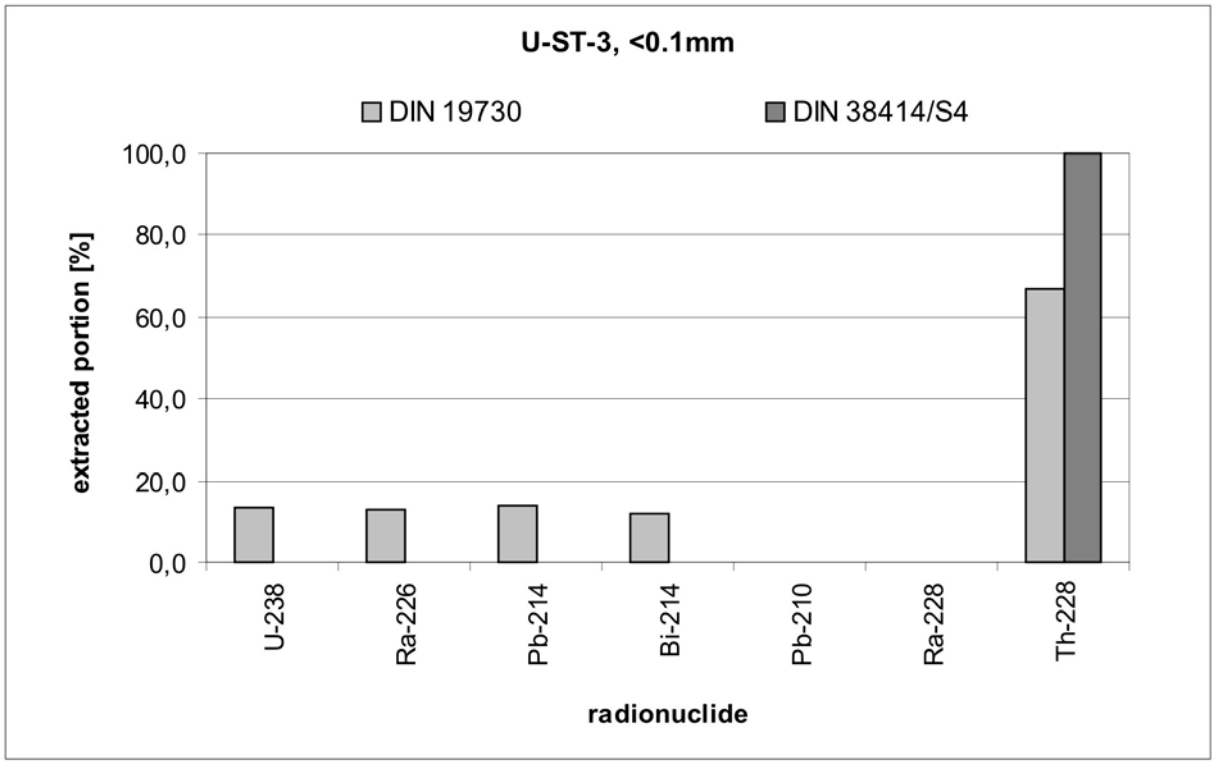

Fig. 5-74: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the stockpile dead rock U-ST-3, <0.1mm.

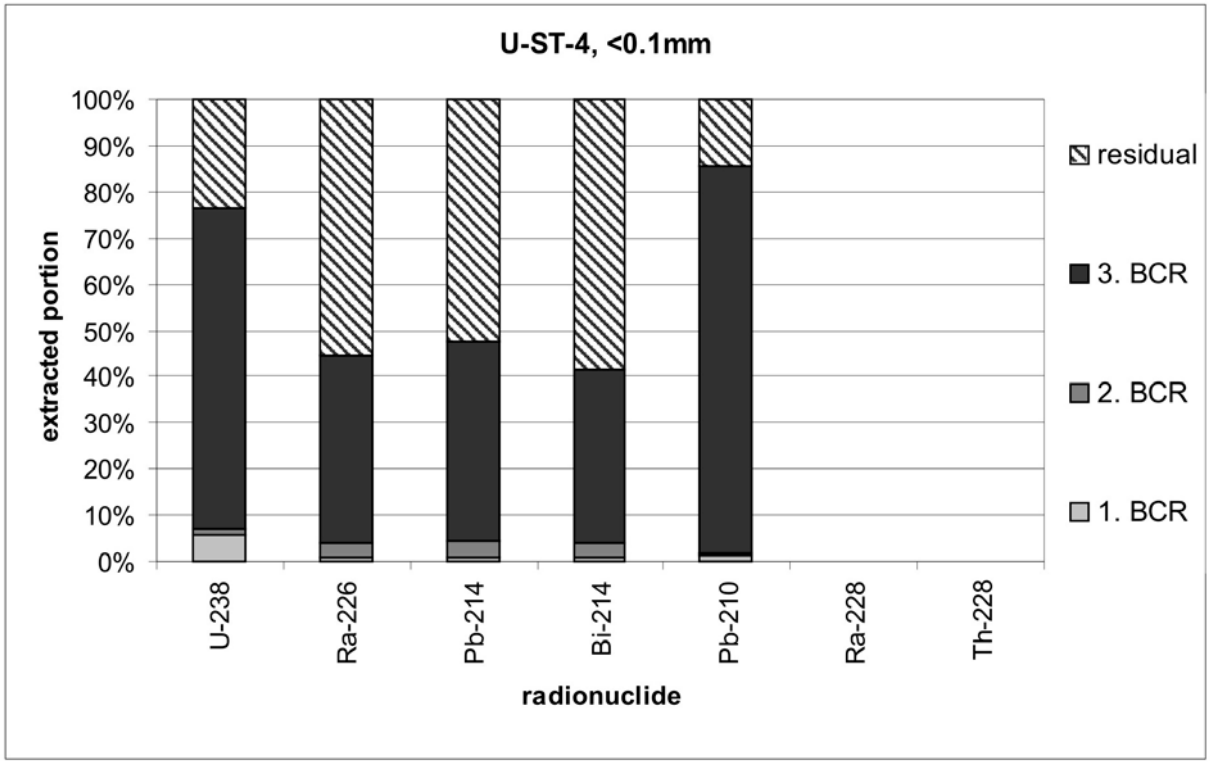

Fig. 5-75: Radionuclide fractions dissolved by BCR-procedure from the stockpile dead rock U-ST-4, <0.1mm.

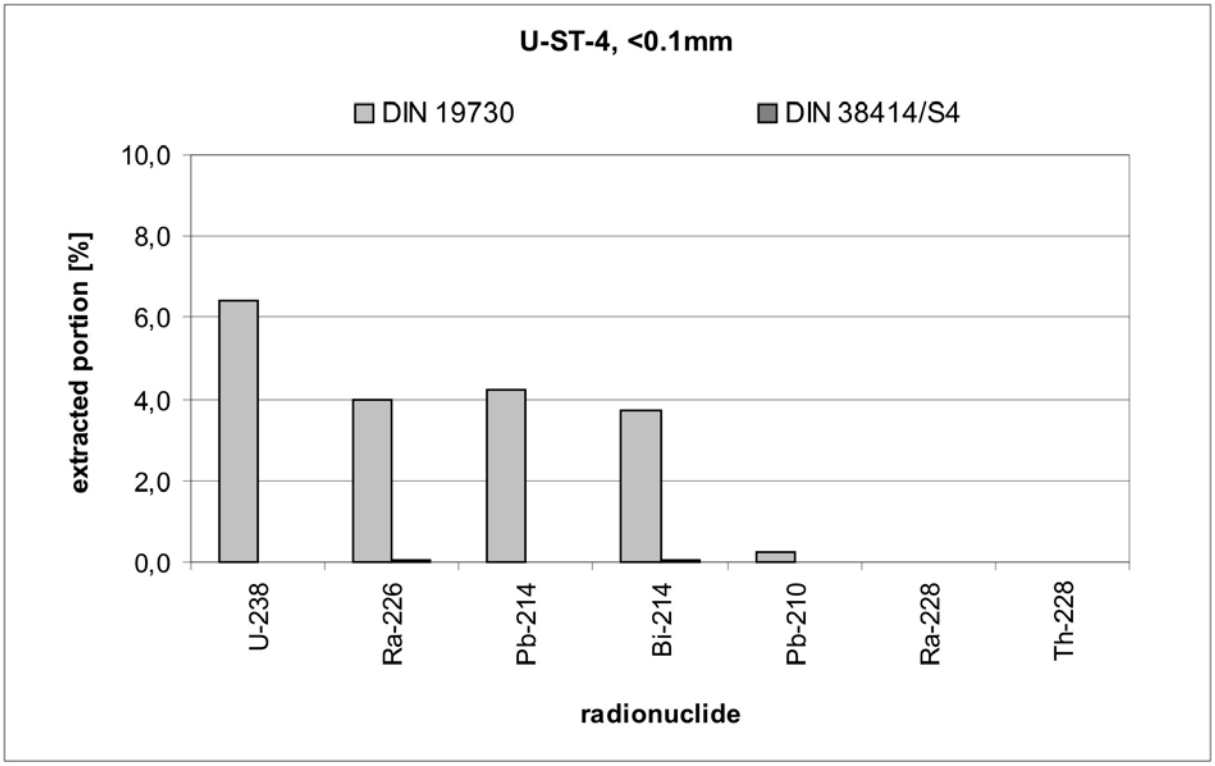

Fig. 5-76: Radionuclide fractions dissolved by DIN 19730 and DIN 38414/S4 from the stockpile dead rock U-ST-4, <0.1mm.

The sediment samples were available in such volumes which allow a separation by grain size into the fractions <2mm and <0.1mm each. As obvious from fig. 5-77, the grain size <2mm of the sediment U-S-5 being unaffected by any uranium mining activity provides only ^{226}Ra from the

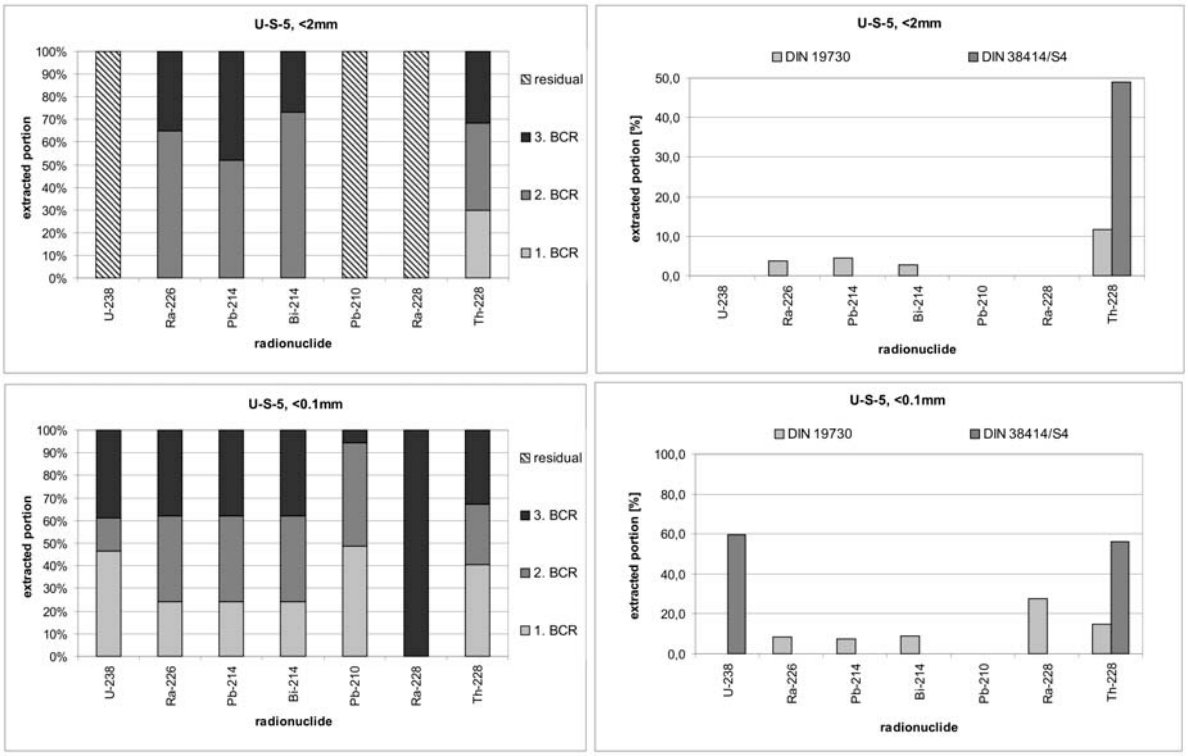

Fig. 5-77: Radionuclide fractions dissolved from the sediment U-S-5 by BCR-procedure, DIN 19730 and DIN 38414/S4 with regard to both grain sizes <2mm and <0.1mm.

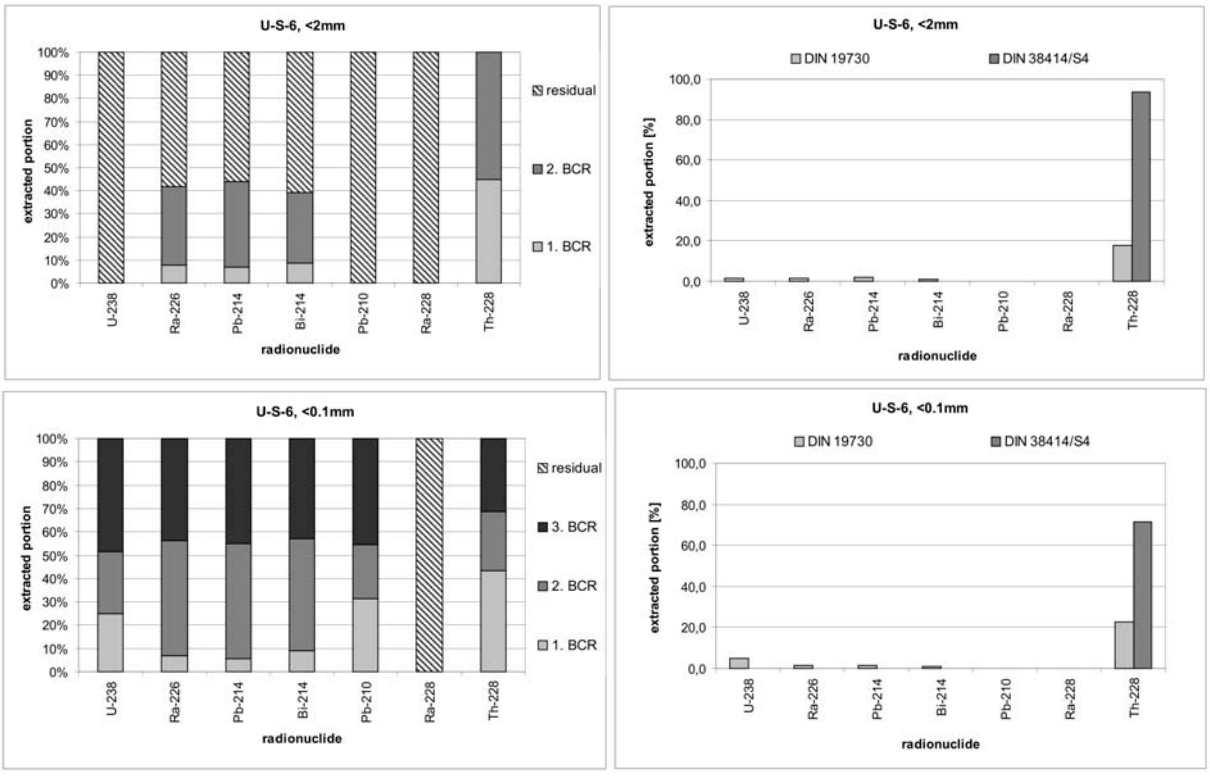

Fig. 5-78: Radionuclide fractions dissolved from the sediment U-S-6 by BCR-procedure, DIN 19730 and DIN 38414/S4 with regard to both grain sizes <2mm and <0.1mm.

uranium decay series from the reducible fraction by 65% and from the oxidisable fraction by 35%, ^{228r}Th is roughly spread among the three BCR extraction liquids by a third. In contrast, the milled aliquote is proven to contain all the relevant radionuclides in almost all the BCR fractions. In the easily exchangeable extract ^{238}U can be found by 47%, ^{226}Ra by 23%, ^{210}Pb by 49% and ^{228r}Th by 41%, the iron and manganese oxides fraction contains ^{238}U by 15%, ^{226}Ra by 39%, ^{210}Pb by 45% and ^{228r}Th by 27% and the organic matter and sulphide fraction is determined to contain ^{238}U by 38%, ^{226}Ra by 38%, too, ^{210}Pb by 6%, all the ^{228}Ra by 100% and ^{228r}Th by 32%. The <2mm grain size provides 4% of ^{226}Ra and 12% of ^{228r}Th for plants, the grain size <0.1mm 9% of ^{226}Ra, 27% of ^{228}Ra and 16% of ^{228r}Th. But in general, the initial sample material does not contain radionuclide concentrations higher than 100Bq/kg.

The second sediment U-S-6, which is taken along the riverside of a tributary being fed by a tailing pond, shows significantly enhanced initial activity concentrations of the uranium decay series' radionuclides (see chapter "5.1.7 Uranium industry"). The grain size <2mm has no radionuclides being bound to organic matter or sulphides, in the easily exchangeable fraction ^{226}Ra is present by 8% and ^{228r}Th by 44%, the oxidisable fraction contains ^{226}Ra by 32% and ^{228r}Th by 56% (fig. 5-78). In the milled fraction, the ratios of the radionulides' types of bounding are as follows, ^{228}Ra was not detected in any of the BCR's extraction liquids:

^{238}U:	24% 1. BCR,	28% 2. BCR,	48% 3. BCR fraction
^{226}Ra:	7% 1. BCR,	49% 2. BCR,	44% 3. BCR fraction
^{210}Pb:	31% 1. BCR,	23% 2. BCR,	46% 3. BCR fraction
^{228r}Th:	43% 1. BCR,	26% 2. BCR,	31% 3. BCR fraction

In contrast, the grain size does not seem to influence the plant availability and water solubility. 4% of the initial ^{238}U, 4% of ^{226}Ra and 17% of ^{228r}Th are plant available from the <2mm fraction, 7% of ^{238}U, 4% of ^{226}Ra and 22% of ^{228r}Th from the <0.1mm fraction. Water leaches only ^{228r}Th by 93% from the grain size <2mm and 70% from <0.1mm.

The waste materials from the uranium extraction processes are represented by four tailing samples, which all were also separated into both grain size fractions <2mm and <0.1mm. The first sample W-T-1 provides all radionuclides for the easily exchangeable fraction from both grain sizes. ^{238}U is solved from <2mm by 30%, ^{226}Ra by 22%, ^{210}Pb by 12%, ^{228}Ra completely by 100% and ^{228r}Th by 26%, the milled material consists of easily exchangeable ^{238}U by 18%, ^{226}Ra by 25%, ^{210}Pb by 21%, ^{228}Ra by 100% and ^{228r}Th by 47% (fig. 5-79). The extraction liquids of the reducible portions of the <2mm fraction only contains ^{226}Ra by 8% and ^{228r}Th by 36%, in the milled version ^{238}U is present by 23%, ^{226}Ra by 23%, ^{210}Pb by 7%, ^{228}Ra by 100% and ^{228r}Th by 47%. 8% of ^{226}Ra and 38% of ^{228r}Th are bound to organic matter and sulphides in the <2mm grain size fraction and these dimensions are also transferable to the milled material accompanied with 7% of ^{210}Pb. The water solubilities and plant availabilities are similarly developed for both grain sizes, ^{238}U is determined to be plant available by 4% from the <2mm fraction and by 43% from the <0.1mm fraction, ^{226}Ra by 26% respectively 38% and ^{228r}Th by 20% respectively 100%. 60% of ^{228}Ra are water soluble from both grain sizes, 36% of ^{228r}Th from <2mm and 60% from <0.1mm fraction.

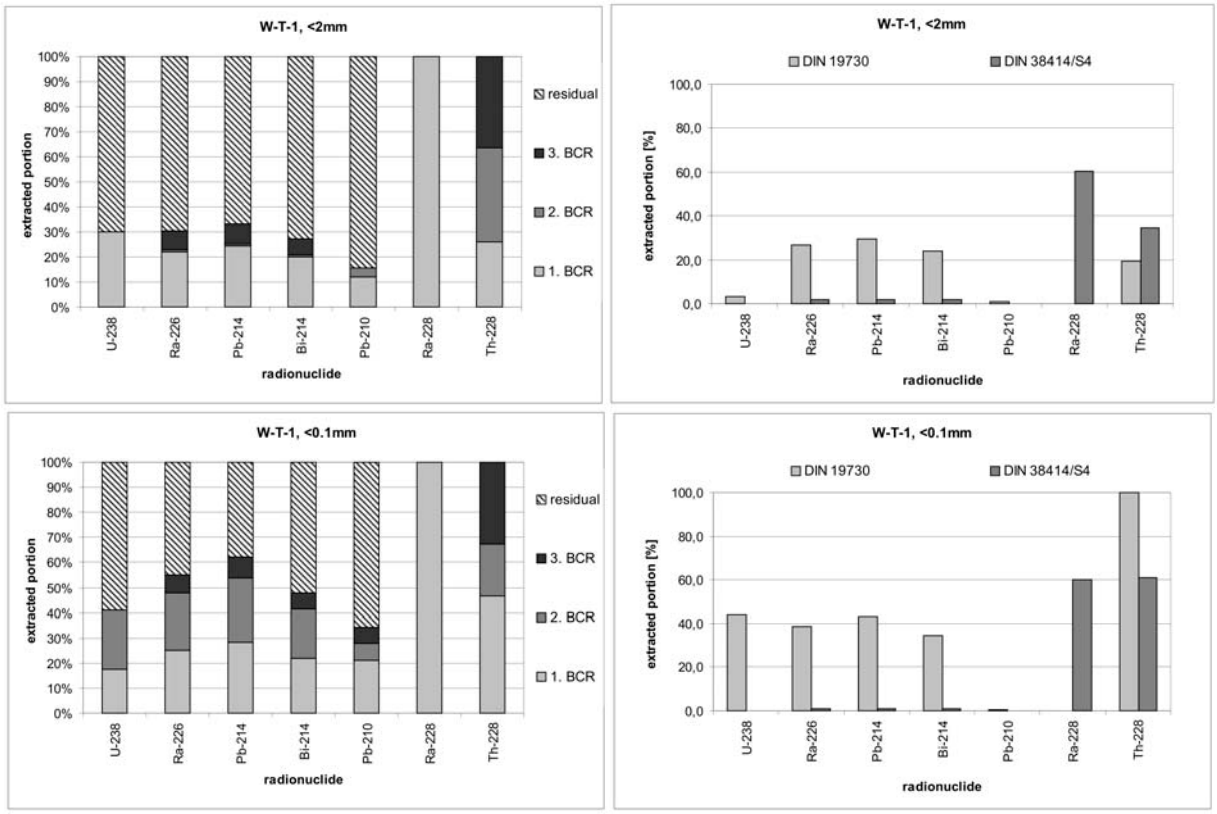

Fig. 5-79: Radionuclide fractions dissolved from the tailing W-T-1 by BCR-procedure, DIN 19730 and DIN 38414/S4 with regard to both grain sizes <2mm and <0.1mm.

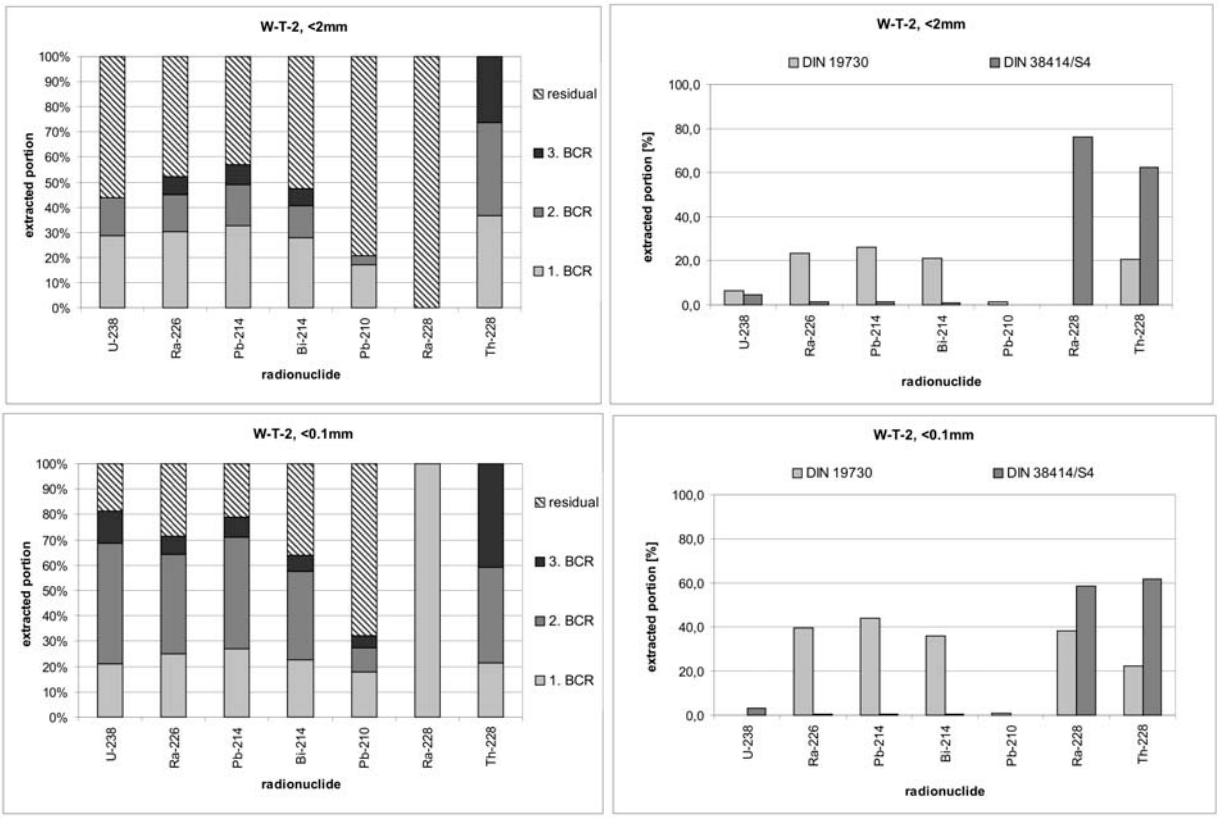

Fig. 5-80: Radionuclide fractions dissolved from the tailing W-T-2 by BCR-procedure, DIN 19730 and DIN 38414/S4 with regard to both grain sizes <2mm and <0.1mm.

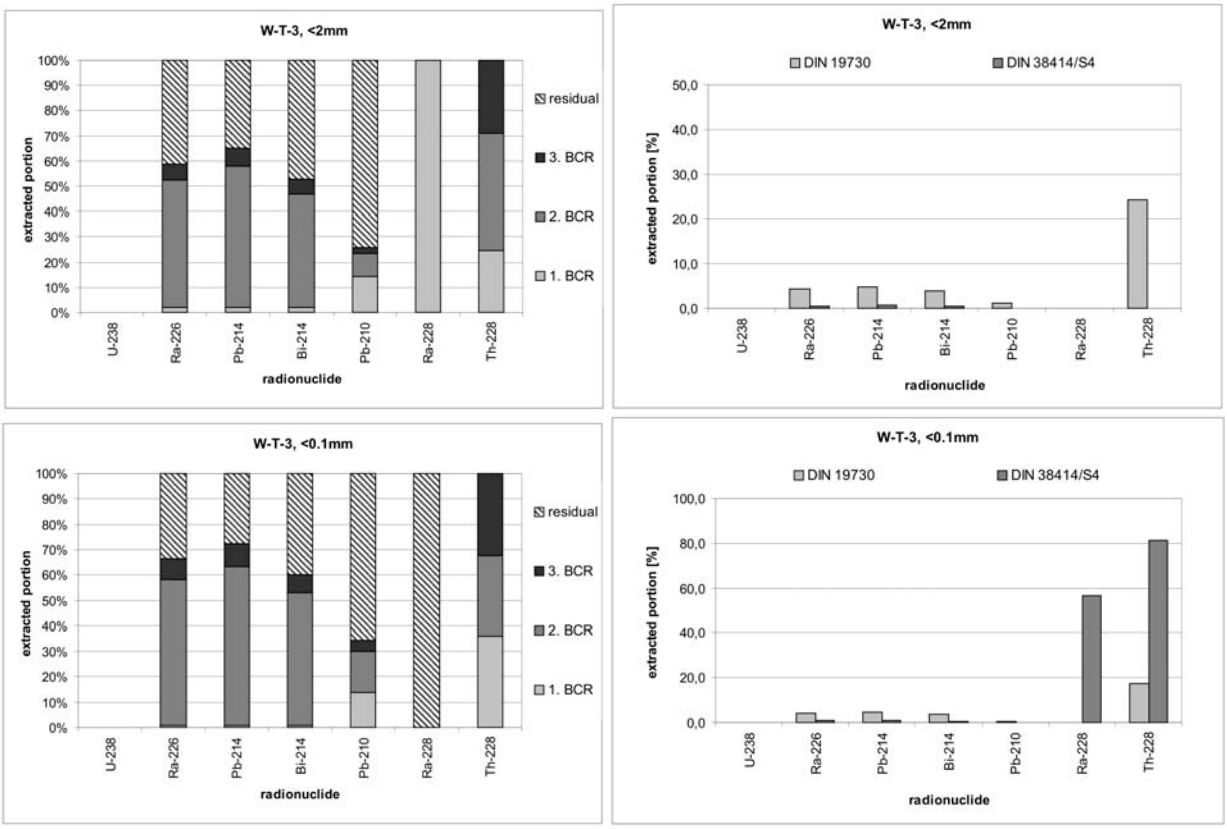

Fig. 5-81: Radionuclide fractions dissolved from the tailing W-T-3 by BCR-procedure, DIN 19730 and DIN 38414/S4 with regard to both grain sizes <2mm and <0.1mm.

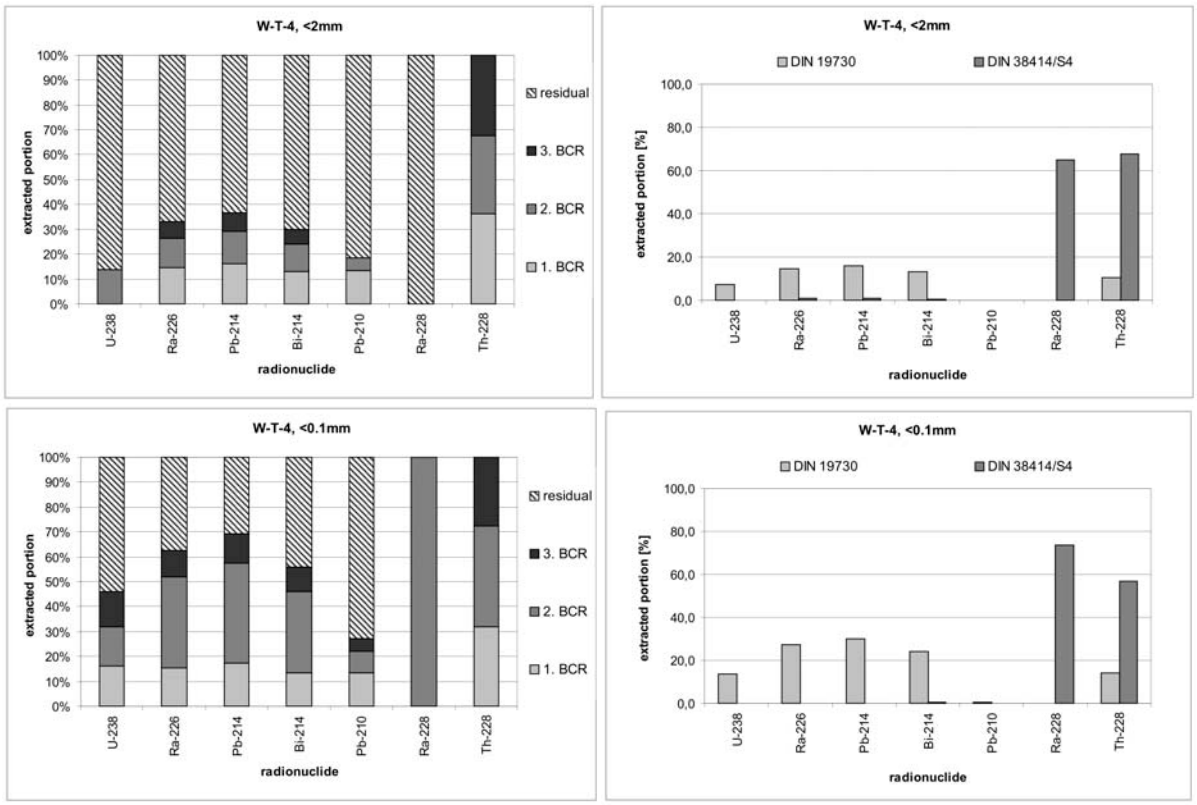

Fig. 5-82: Radionuclide fractions dissolved from the tailing W-T-4 by BCR-procedure, DIN 19730 and DIN 38414/S4 with regard to both grain sizes <2mm and <0.1mm.

The second tailing sample W-T-2 provides ^{238}U (28%), ^{226}Ra (30%), ^{210}Pb (17%) and ^{228}Th (36%) from the <2mm fraction for the easily exchangeable portion, the <0.1mm grain size consists of easily echangeable ^{238}U by 21%, ^{226}Ra by 25%, ^{210}Pb by 18%, the complete initial ^{228}Ra content and ^{228}Th by 21% (fig. 5-80). The fractions being bound to iron and manganese oxides contain 14% ^{238}U, 13% ^{226}Ra, 7% ^{210}Pb and 37% ^{228}Th from the initial <2mm grain size's activity concentrations. The milled material is proven to carry 48% of ^{238}U, 38% of ^{226}Ra, 8% of ^{210}Pb and 38% of ^{228}Th bound to iron and manganese oxides. In the <2mm oxidisable fraction, no uranium, lead and ^{228}Ra can be found, but ^{226}Ra is present by 8% and ^{228}Th by 27%. From the <0.1mm grain size, 12% of ^{238}U, 9% of ^{226}Ra, 5% of ^{210}Pb and 41% of ^{228}Th were leached as being bound to organic matter and sulphides. 6% of the initial ^{238}U content, 16% of ^{226}Ra and 21% of ^{228}Th are determined to be plant available from the <2mm grain size, the <0.1mm fraction does not provide any uranium, but ^{226}Ra by 40%, ^{228}Ra by 38% and ^{228}Th by 22%. The water solubility is developed in similar volumes for both grain sizes, roughly 5% of uranium, 77% (<2mm) respectively 59% (<0.1mm) of ^{228}Ra and 62 % of ^{228}Th each are water soluble.

A slightly different picture is given by the third sample W-T-3. Since uranium is not measured in the extraction procedures' starting material, it is also not detected in any of the liquids. The easily exchangeable fraction just dissolved 2% of ^{226}Ra from the <2mm grain size, the <0.1mm fraction does not contain any, 14% of ^{210}Pb each and 24% respectively 36% of ^{228}Th, but ^{228}Ra by 100% from the <2mm grain size (fig. 5-81). More than 50% of ^{226}Ra are bound to iron and manganese oxides in both grain sizes, lead by 8% (<2mm) and 17% (<0.1mm) and ^{228}Th by 47% (<2mm) and 30% (<0.1mm). In the oxidisable fraction ^{226}Ra is present by 6% from <2mm and 7% from <0.1mm grain size, lead by 3% and 5% and ^{228}Th by 27% and 34%. 5% of the ^{226}Ra content from both material fractions, 2% of ^{210}Pb (<2mm) and 24% respectively 18% of ^{228}Th are available for plants. The water solubility is only object for the milled material fraction, 57% of ^{228}Ra and 81% of ^{228}Th are determined in that extraction liquid.

The last tailing sample W-T-4 provides 14% of ^{226}Ra, 13% of ^{210}Pb and 36% of ^{228}Th for the easily exchangeable extraction step from the <2mm grain size fraction, 13% of ^{238}U, 11% of ^{226}Ra, 4% of ^{210}Pb and 31% of ^{228}Th are bound to iron and manganese oxides (fig. 5-82). The oxidisable fraction is proven to have only solved 5% of ^{226}Ra and 33% of ^{228}Th. ^{228}Ra was not detected in any of the <2mm grain size BCR extraction liquids. The radionuclide portions dissolved from the <0.1mm fraction are determined in following dimensions:

^{238}U:	16% 1. BCR,	16% 2. BCR,	14% 3. BCR fraction
^{226}Ra :	16% 1. BCR,	36% 2. BCR,	11% 3. BCR fraction
^{210}Pb:	13% 1. BCR,	8% 2. BCR,	4% 3. BCR fraction
^{228}Ra :		100% 2. BCR fraction	
^{228}Th:	32% 1. BCR,	40% 2. BCR,	28% 3. BCR fraction

In the plant available extract resulting from the <2mm grain size, 8% of ^{238}U, 16% of ^{226}Ra and 11% of ^{228}Th are found. The leaching volumes from the milled material are slightly enhanced, 16% of ^{238}U, 36% of ^{226}Ra and 16% of ^{228}Th are available for plants. The water solubility is developed in similar dimensions for both grain sizes. Only the ^{232}Th progenies ^{228}Ra and ^{228}Th are

present in the that leaching fraction, ^{228}Ra by 65% (<2mm) respectively 72% (<0.1mm) and ^{228}Th by 67% (<2mm) and 57%.

In summary, the different materials from uranium mining and processing show, of course, also some differences in their radionuclides' types of bounding. In case of the raw materials and dead rocks being heaped up in stockpiles as well, the type of rock defines the chemical leaching behaviours. Even the uranium ore bearing sandstones differ significantly, on the one hand almost all the contained uranium and lead, but no radium was leached by the BCR procedure, on the other not all the uranium, but similar portions of all the uranium decay series' radionuclides are proven in those extraction liquids. The slags do not contain initial activity concentrations higher than 200Bq/kg (therefore no TENORM) indeed, but they show radium and lead remaining in the residual, whereas uranium is mostly bound to oxides and also well soluble in water. Both the pegmatite and the sandstone breccia are characterised by the very most of all the uranium decay series' radionuclides being bound to organic matter and sulphides. The sediments vary in their predominating radionuclides' type of bounding, but especially the grain size fraction <2mm of the contaminated one U-S-6 provides a third of the initial radium content under reducible conditions. The grain size's influence is well shown on the tailings waste materials, which all were separated into <2mm and <0.1mm fractions. The most of the uranium decay series' radionuclides are easily exchangeable respectively bound to iron and manganese oxides and the <0.1mm fraction almost always provides the bigger portions available for plants and within the BCR extraction procedure. In contrast, the tailings' water solubility does not seem to be influenced significantly by that parameter and only affects the ^{232}Th progenies by a leaching factor of roughly 60%.

5.3 Radon emanation rates

The radon emanation rates were mainly measured from the <2mm grain size, because that is the representative fraction for the granular materials. The milled fractions were only used from hard rocks or additionally if enough material volume was available. Unfortunately, the hard coal sample volumes and also that of the uranium ore R-UO-2 were too small for reliable measurements. The thorium samples were excluded due to the significantly interfering by the short living ^{220}Rn. The given uncertainties of the absolute rates were calculated as described in chapter "4.6.4 Total uncertainty of radon emanation". The presented percentages are quoted to the respective initial ^{226}Ra content (see chapter "5.1 Initial radionuclide content"), which is therefore called emanation coefficient and decribes the volatile loss from the uranium decay series.

5.3.1 Phosphate industry

All the emanation rates were measured from the samples' grain size <2mm (fig. 5-83). The highest rate is determined by 22Bq/kg for the Moroccan sedimentary phosphate ore, but that is put into perspective by the corresponding low emanation coefficient of 1.7% due to the high

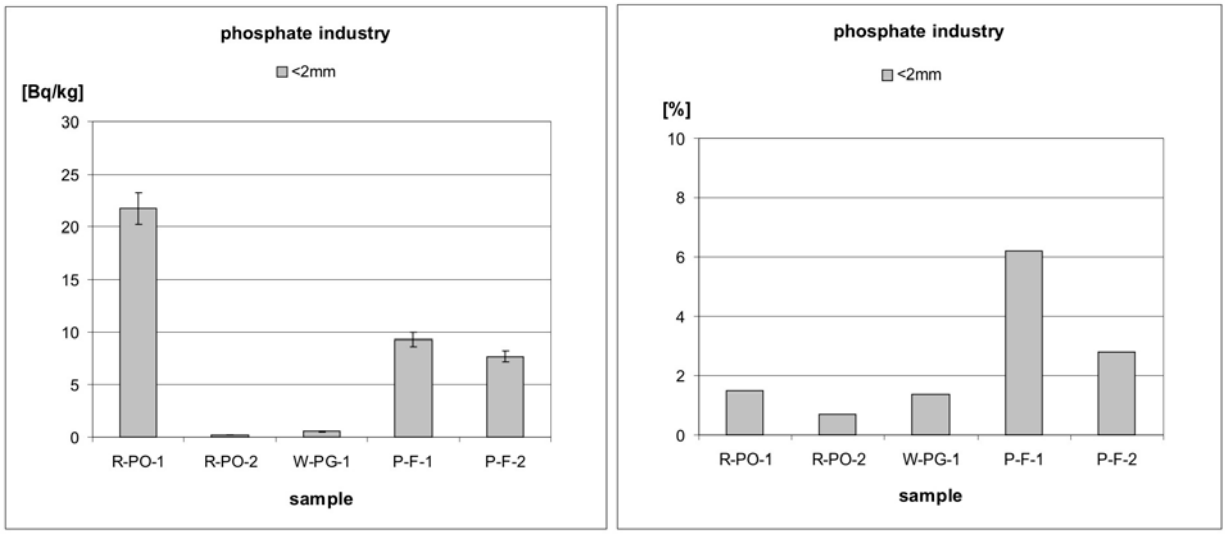

Fig. 5-83: Radon emanation of all phosphate industry's materials; left: emanation rates, right: emanation coefficients.

initial ^{226}Ra content. Both the Kola phosphate ore and the phosphogypsum waste show emanation rates lower than 1Bq/kg being in accordance to coefficients of 1% roughly, whereas the fertilisers have some rates ranging between 8 and 9.5Bq/kg. That results in an emanation coefficient of 6% for the NPK-fertiliser (P-F-1) and 3% for the PK-fertiliser (P-F-2) respectively.

5.3.2 Aluminium industry

The materials resulting from aluminium production were available in sufficient volumes for separating into both grain size fractions <2mm and <0.1mm. Concerning the aluminium ores' emanation rates, there is a wide discrepancy between that of the Boke zone (R-AO-1) ranging around 12Bq/kg for both grain sizes and that of the Trombeta deposit (R-AO-2), which is determined in huge dimensions by 210Bq/kg for the sieved fraction and 147Bq/kg for the milled one (fig. 5-84). The red sludge waste W-RS-1 just emanates relatively low radon concentrations of

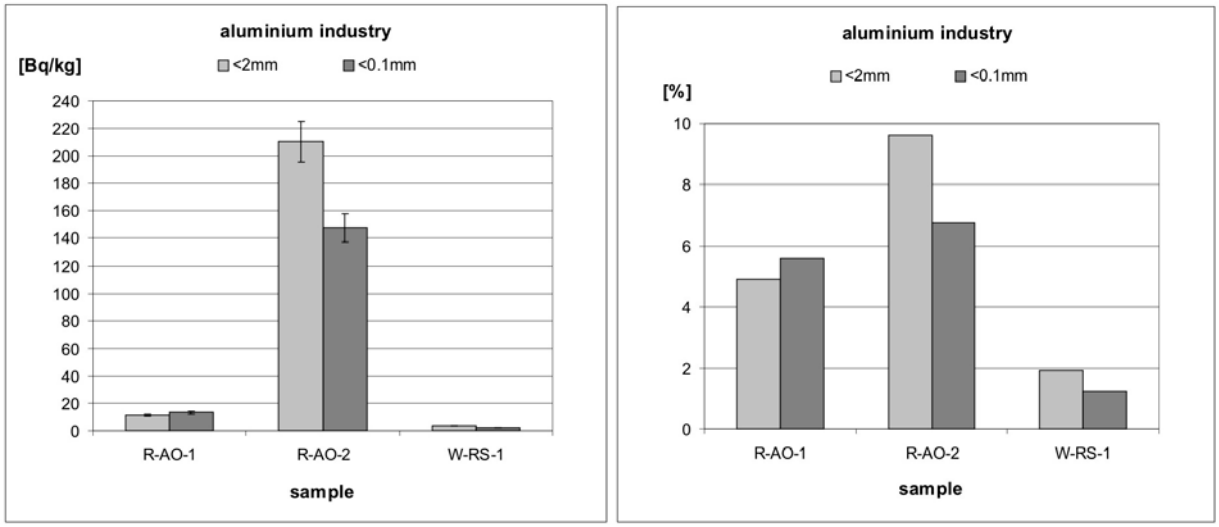

Fig. 5-84: Radon emanation of all aluminium industry's materials; left: emanation rates, right: emanation coefficients.

roundabout 3Bq/kg in each case. The respective emanation coefficients are given by 5.5% roughly for the Boke aluminium ore, whereas the <2mm fraction of the Trombeta bauxite shows the highest coefficient of almost 10%, that of the <0.1mm grain size is slightly smaller by 6.5%. The red sludge emanates 2% from the <2mm fraction and 1.3% from the milled fraction.

5.3.3 Refractory industry

The refractory's raw material zircon sand R-ZS-1 and the fused zirconia mullite P-FZM-1 as well were separated into both the grain size fractions <2mm and <0.1mm, the filter dust W-FD-1 and the second mullite P-FZM-2 were just measured for the milled fraction. The sieved fraction of R-ZS-1 is determined for an emanation rate of 2.5Bq/kg, the milled one for the double (fig. 5-85). The calculated emanation coefficients amount to 0.08% and 0.16% respectively. The filter dust emanates 0.4Bq/kg corresponding to 0.13%. The <2mm fraction of P-FZM-1 does not show any emanating radon, but the <0.1mm is proven for almost 1Bq/kg, which is equal to a coefficient of 0.06%. That of the second sample P-FZM-2 is given by 0.08% resulting from an emanation rate of 3.3Bq/kg.

5.3.4 Crude oil exploitation

Both material types, the sludge and the scales, are available for their <2mm fraction. The two sludge samples generally show really high emanation rates by 120Bq/kg and 570Bq/kg, which corresponds to emanation coefficients of 0.7% and 1.2% (fig. 5-86). The scales' emanation rates are proven for 50Bq/kg and 30Bq/kg, which means emanation coefficients of 1.3% and 0.4% respectively.

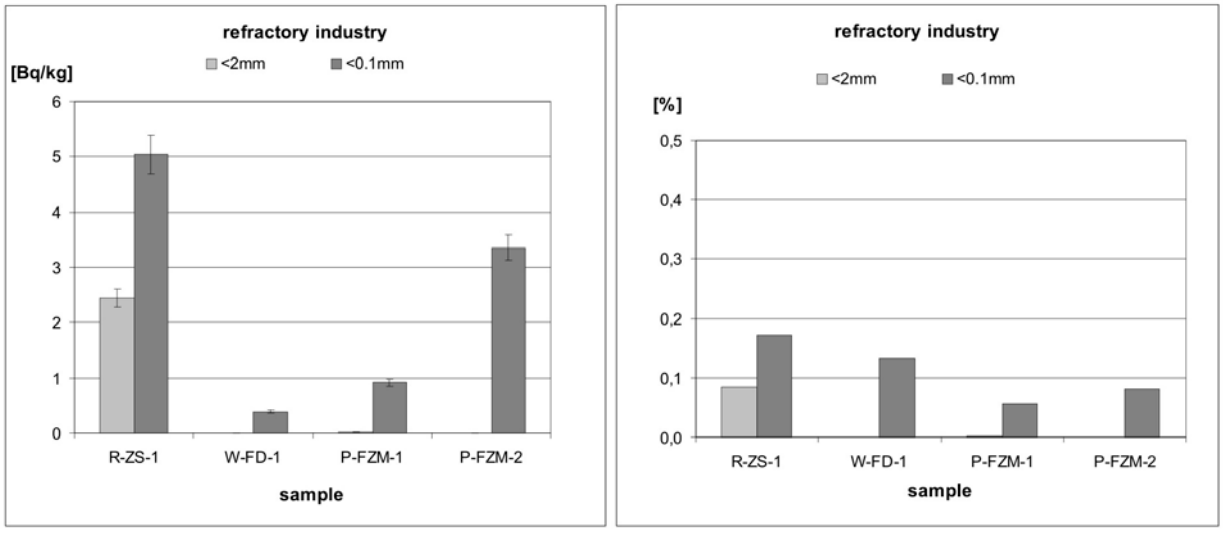

Fig. 5-85: Radon emanation of all refractory industry's materials; left: emanation rates, right: emanation coefficients.

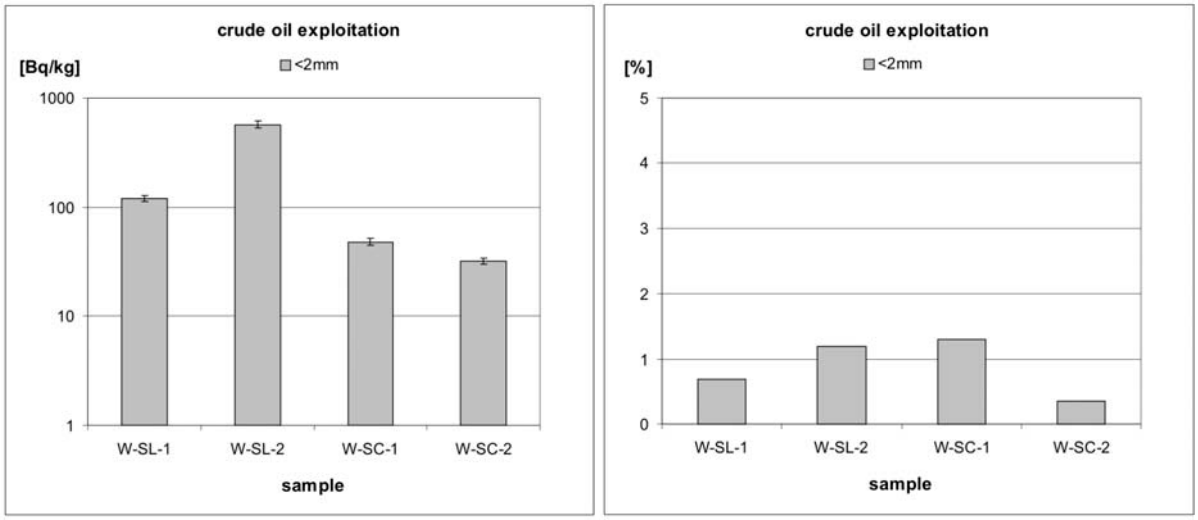

Fig. 5-86: Radon emanation of all crude oil exploitation's materials; left: emanation rates, right: emanation coefficients.

5.3.5 Uranium industry

From the uranium industry, the most samples were available and their specific radon emanation is determined from that grain size as they occur. The milled fraction of the hard rock R-UO-1 is measured for the absolutely highest emanation rate by 2395Bq/kg, which corresponds to an emanation coefficient of 2.6% (fig. 5-87). The tailings' W-T-1 and W-T-2 emanate radon in similar dimensions of 84Bq/kg and 113Bq/kg, W-T-3 shows a higher value of 200Bq/kg, whereas the fourth tailing sample is detected for 39Bq/kg. But in consequences, all the resulting coefficients range around 2%, that of W-T-1 is given by 2.4%, of W-T-2 by 1.5%, of W-T-3 by 2% and of W-T-4 by 1.3%. The unwanted by-products heaped up on stockpiles vary significantly in their radon emanation characteristics. Both the slags U-ST-1 and U-ST-2 do not show any mentionable emanating radon (fig. 5-88), but the dead rocks do. U-ST-3 is characterised by an emanation rate of almost 31Bq/kg leading to a coefficient of 1.5%, the rate of the uranium bearing dead rock U-ST-4 of 22Bq/kg results only in a negligible coefficient near zero due to the

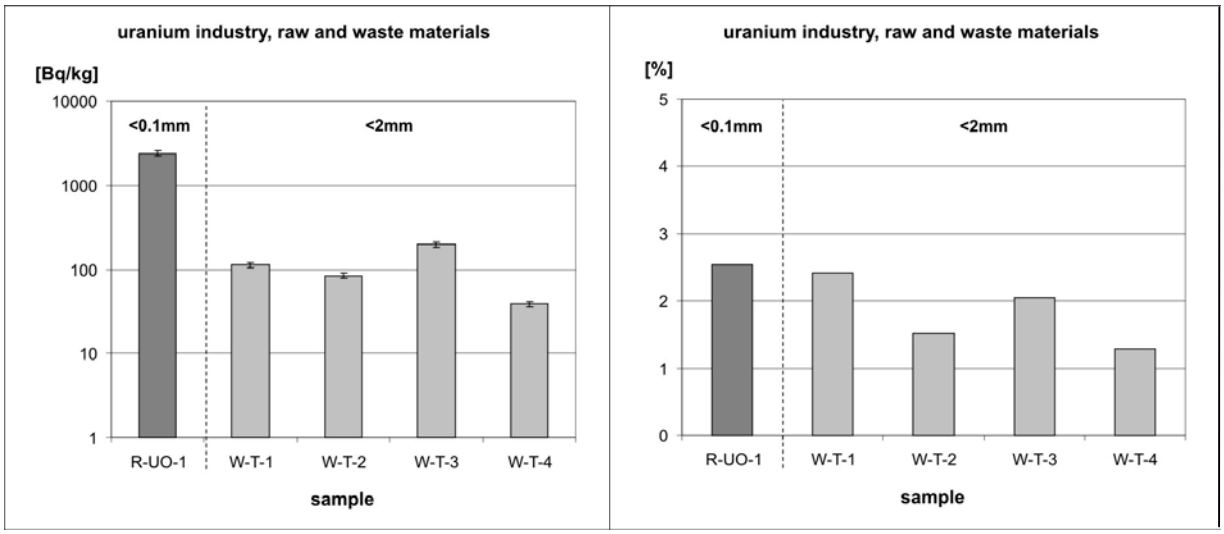

Fig. 5-87: Radon emanation of the uranium industry's raw and waste materials; left: emanation rates, right: emanation coefficients.

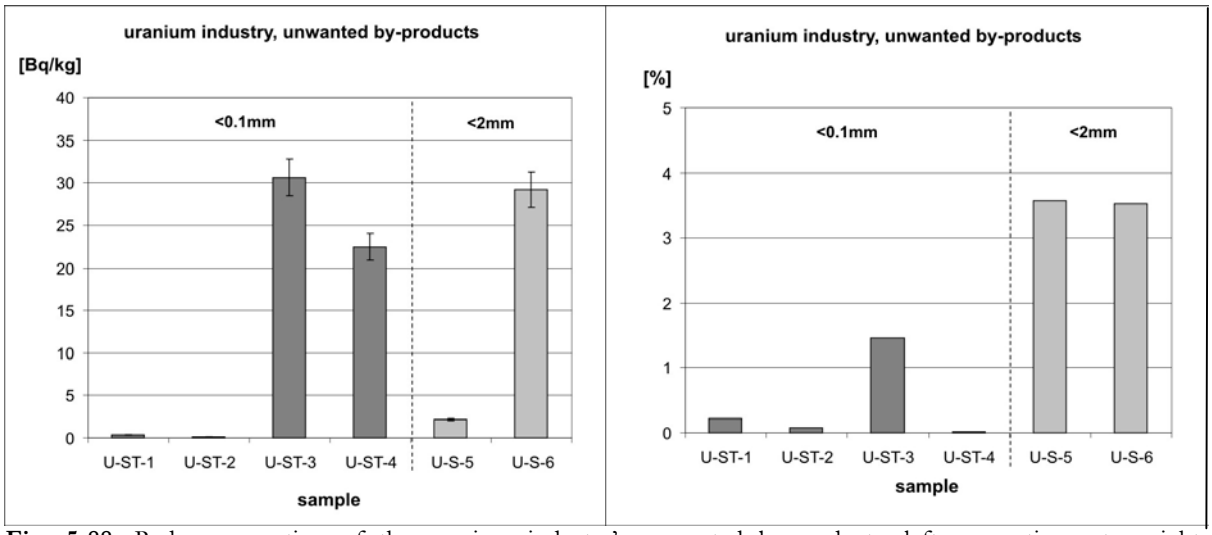

Fig. 5-88: Radon emanation of the uranium industry's unwanted by-products; left: emanation rates, right: emanation coefficients.

immense initial ^{226}Ra concentration. The sediments, U-S-5 as an unaffected one and U-S-6 representing a mining influenced one, show both the same emanation coefficients of 3.5%. That is caused by their absolutely different emanation rates compared with their also deviating radium contents, U-S-5 is detected for 2Bq/kg and U-S-6 for 29Bq/kg.

5.3.6 Summary

In summary it must be pointed out, that the highest radon emanation rate of more than 2300Bq/kg is given by the milled uranium ore bearing breccia R-UO-1, but also the sludge resulting from crude oil exploitation and the Trombeta bauxite emanate a few hundreds Bq/kg. The very most of the materials are proven for emanation rates in the range of some tens Bq/kg, those of the phophate and refractory production show the lowest dimensions. Nevertheless, the highest emanation coefficients of maximum 10% result from the phosphate product NPK-fertiliser and the Trombeta bauxite once again, usually they are in the range less than 5%, especially the refractory's materials show less than 0.2%.

5.4 Gamma dose rates

The gamma dose rates were measured at those sites, which have been directly accessible. Therefore, only the hard coal mining influenced, thorium and uranium containing samples are presented. All the respective gamma dose rates are summarised in table 5-2 and explained in detail in the following chapters.

Table 5-2: Gamma dose rates taken at all directly accessible sites.

industry	sample	location	gamma dose rate [nSv/h]
hard coal mining	U-S-1	irregularly affected flood plain soil	280
	U-S-2	unaffected riverside area (background)	130
	U-S-3	slip-off slope	400
	U-S-4	undercut slope	340
thorium compounds industry	U-SO-1	thorium-cobalt catalyst residue	37,000
	U-SO-2	thorium containing dust	1350
	U-SO-3		1000
	U-SO-4		1000
uranium industry	R-UO-1	outcropping rock layer	800
	R-UO-2		900
	U-ST-1	stockpiles (CZ)	150
	U-ST-2		200
	U-ST-3		500
	U-ST-4		1500
	W-T-1	tailing pond (SL)	1700
	W-T-2		2200
	W-T-3		4500
	W-T-4		3000

5.4.1 Hard coal extraction

The locations of the sediments' sampling points can be drawn from fig. 3-9. U-S-1 represents a flood plain soil being irregularly affected by flood events, the gamma dose rate was about 280nSv/h, whereas U-S-2 is taken from an unaffected area as background sample showing a gamma dose rate of 130nSv/h. U-S-3 and U-S-4 are taken at the riverside close to the waterline, the first one from slip-off slope (gamma dose rate: 400nSv/h), the latter at undercut slope (gamma dose rate: 340nSv/h).

5.4.2 Thorium compounds industry

At the site where the residues of thorium-cobalt catalysts were disposed, the by far highest gama dose rate of 37,000nSv/h is detected for the sample U-SO-1. The other three soil samples derived from the other site being contaminated by thorium bearing dust show very similar gamma dose rates of roundabout 1200nSv/h.

5.4.3 Uranium industry

Both the raw materials R-UO-1 and R-UO-2 for the Slovenian uranium processing industry show corresponding gamma dose rates of 800nSv/h and 900nSv/h respectively, which is a hint for the hard rocks' interspersing by uranium. The stockpile samples were taken close to Pribram, Czech Republic, as shown in fig. 3-12 and vary widely in their gamma dose rates. Both the sampling points of the slags U-ST-1 and U-ST-2 are characterised by only slightly enhanced rates of 150nSv/h and 200nSv/h respectively. That of the pegmatite U-ST-3 is determined for 500nSv/h and the ground of the uranium ore bearing dead rock is classified for strongly enhanced 1500nSv/h. That means, the gamma dose rates measured on stockpiles can differ widely in a ten of potency. In contrast, the tailing waste materials from the only Slovenian settling pond are determined in similar dimensions of a few thousands of nSv/h, the minimum is given by 1700nSv/h and rises up to a maximum of 4500nSv/h.

6 Discussion

6.1 Rating and classification of the solid initial TENORM samples

The total of 36 solid initial TENORM samples are separated according to their positions in the production processes, i.e. by type of material (raw material, waste material, unwanted by-products or products). The material groups are further classified by 5 activity concentration limits for each of the 7 relevant radionuclides.

6.1.1 Raw materials

In frame of this thesis, 7 raw material samples are investigated. As obvious from figure 6-1, their uranium contents cover the whole range from "lower than 50Bq/kg" up to "between 100,000 and 1,000,000Bq/kg" with a slight accentuation on the highest concentrations. In contrast, the ^{226}Ra and progenies and ^{210}Pb concentrations as well mainly range "between 1000 and 100,000Bq/kg", whereas the ^{232}Th progenies exceed the 200Bq/kg limit only in the case of zircon sand R-ZS-1 (fig. 5-6).

According to the classification system proposed by the German Commission on Radiation Protection for residual areas affected by uranium mining in the former GDR (SSK, 1992), which is presented in figure 2-1, only the phosphate ore R-PO-2 from the Russian Kola peninsula (fig. 5-1) can be excluded from regulations, all the others must be kept under control and mostly in the highest level due to activity concentrations higher than 1000Bq/kg. The application of the second classification system developed in frame of TENORMHARM (fig. 2-2) leads at least to category 2, which means observation, if a low volume of less than 20 tons and only a few people are affected. But this is a "best case" scenario and in practise especially bigger amounts, sometimes also more than 20 affected people which means workers, must be taken for being affected. That would result in the highest category 3, which demands for case studies and/or intervention actions. The exact number of affected workers is impossible to indicate, because the companies usually do not provide detailed information like that about their production processes. The amounts of raw materials can be generally taken for some thousands of tons as reported by PENFOLD et al. (1999), because all the investigated industry types are based on mass productions.

6.1.2 Waste materials

The number of waste material samples is given by 11, of which more than a half show uranium activity concentrations lower than 50Bq/kg (fig. 6-2). This ratio is reversed in the case of the ^{226}Ra and progenies activity concentrations, two thirds are classified to contain more than 1000Bq/kg, the filter dust sample W-FD-1 exceeds even 100,000Bq/kg for ^{210}Pb (fig. 5-7). Both the radionuclides of the ^{232}Th decay series are equally spread on the classes "below 200Bq/kg" and "between 200 and 100,000Bq/kg".

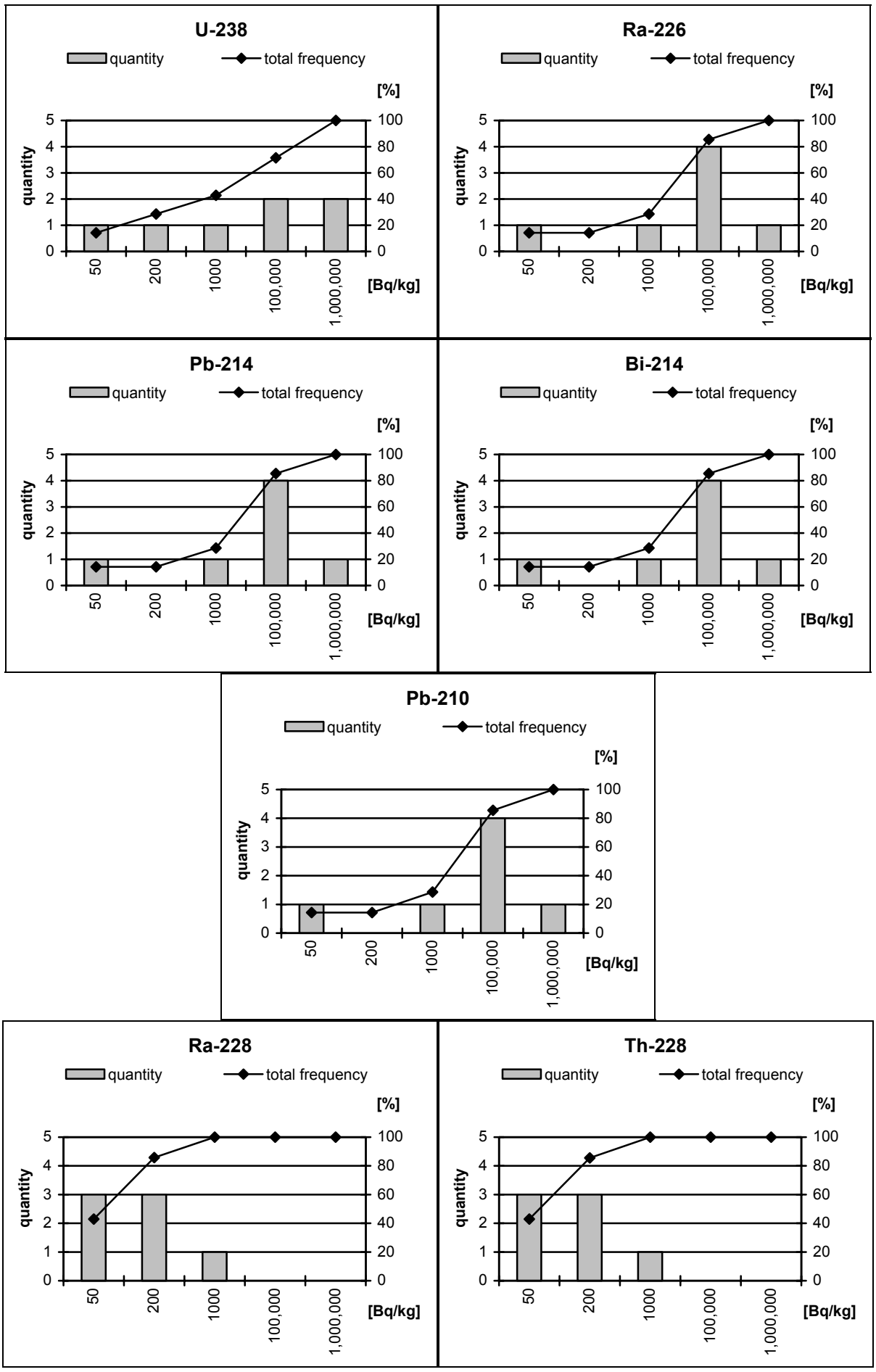

Fig. 6-1: Quantities and total frequencies of the 7 raw materials classified by 5 activity concentration limits for each of the relevant radionuclides.

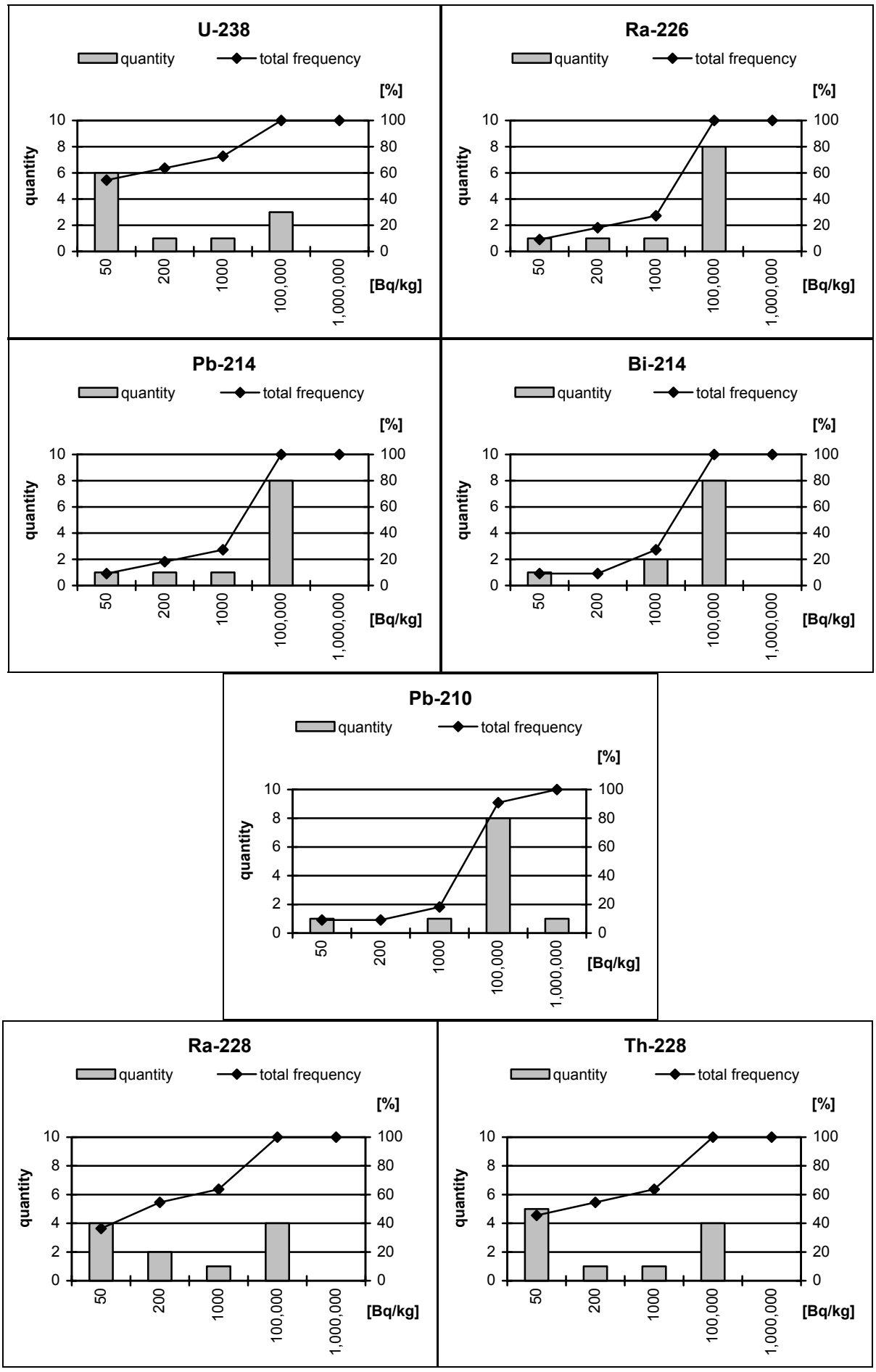

Fig. 6-2: Quantities and total frequencies of the 11 waste materials classified by 5 activity concentration limits for each of the relevant radionuclides.

A classification based on the system of the German Commission on Radiation Protection (fig. 2-1) turns the phosphogypsum sample W-PG-1 out of any regulations due to its activity concentrations of constantly below 200Bq/kg (fig. 5-2), whereas the red sludge W-RS-1 must be regulated in a lower level for its radionuclide contents in the range between 200Bq/kg and 1000Bq/kg (fig. 5-5). All the other wastes exceed the 1000Bq/kg limit in at least one case and must be treated by higher regulations. Apart from W-PG-1, the TENORMHARM classification system (fig. 2-2) also results in the third category "interventions must be undertaken" even if less than 20 persons are affected, because the generated amounts of waste materials are generally higher than 20 tons (PENFOLD et al, 1999). Concerning the filter dust of the refractory production that value might be underbidden, but due to the immense activity cocentration of more than 100,000Bq/kg of ^{210}Pb (fig. 5-7) that substance should also be supervised in the highest category.

6.1.3 Unwanted by-products

The most of the samples (14) are to be declared as "Unwanted by-products". The radionuclide distributions within those materials are quite heterogeneous as obvious from figure 6-3. The uranium concentrations vary from "below 200Bq/kg" for 8 samples, but also 5 specimen contain more than 1000Bq/kg. The ^{226}Ra and progenies activity concentrations are equally spread among all the 5 classes with a slight accentuation on the group "between 1000Bq/kg and 100,000Bq/kg", whereas the ^{210}Pb concentrations are absolutely constantly distributed. In contrast, ^{228}Ra and ^{228}Th show a concentration on the classes "below 200Bq/kg", but nevertheless 3 samples do contain activity concentrations "between 1000Bq/kg and 1,000,000Bq/kg".

The classification according to the German Commission on Radiation Protection (fig. 2-1) characterises the samples U-S-1 (fig. 5-11), U-S-5 (fig. 5-15), U-SO-4 (fig. 5-12), U-ST-1 and U-ST-2 (fig. 5-14) for no need of regulation. Two samples, U-S-2 (fig. 5-11) and U-S-6 (fig. 5-15), demand for a low level regulation, so that all the other 7 samples must be regulated by a higher level. For the reasons as described above, the TENORMHARM classification system classifies all the 9 unwanted by-products "higher than 200Bq/kg" into category 3 "interventions must be undertaken", because the volumes present in the environment are absolutely higher than 20 tons. In case of the stockpiles, the number of persons can be assumed for being lower than 20, but the areas where the sediments and soils are derived from are more frequently visited, especially by children as mentioned by SCHMIDT (2001).

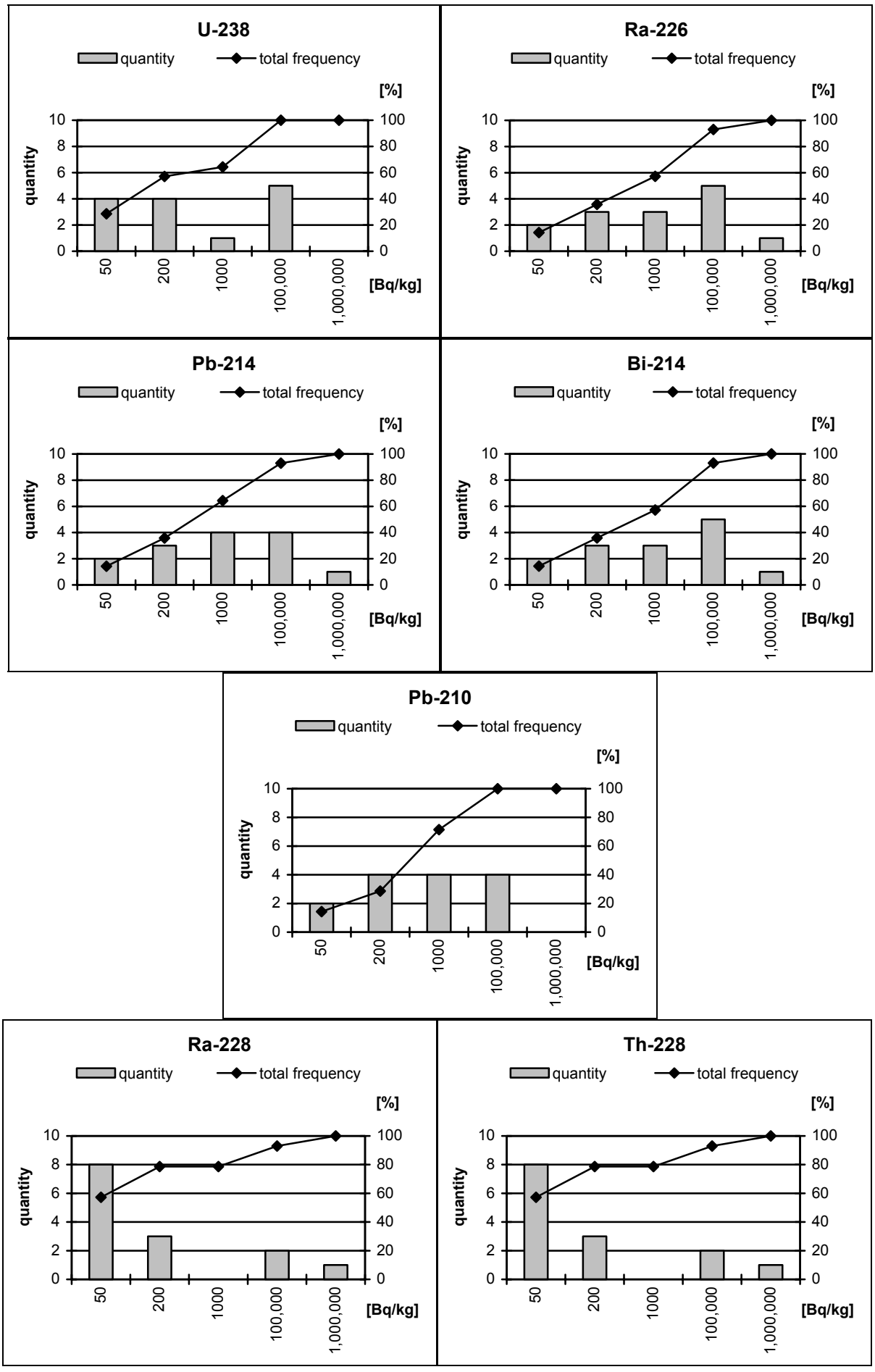

Fig. 6-3: Quantities and total frequencies of the 14 unwanted by-products classified by 5 activity concentration limits for each of the relevant radionuclides.

6.1.4 Products

The products are the smallest group, 4 samples are part of it. 50% of them contain uranium activity concentrations between 200Bq/kg and 1000Bq/kg, the other 50% range between 1000Bq/kg and 100,000Bq/kg (fig. 6-4). The ^{226}Ra and progenies concentrations are slightly different distributed, one sample in each of the classes "below 200Bq/kg" and "below 1000Bq/kg", 50% are classified for "between 1000Bq/kg and 100,000Bq/kg". The ^{210}Pb content is focused on the range "between 1000Bq/kg and 100,000Bq/kg", only that of P-F-1 is below 200Bq/kg (fig. 5-3). Both the ^{232}Th progenies are equally concentrated on "below 50Bq/kg" and "between 200Bq/kg and 1000Bq/kg".

Since all the samples' radionuclide concentrations exceed in at least one case the 200Bq/kg limit, regulations are necessary as proposed by the German Commission on Radiation Protection (fig. 2-1). The fertiliser samples P-F-1 and P-F-2 need a low level regulation, because both underbid the 1000Bq/kg limit (fig. 5-3), but the fused zirconia mullite products P-FZM-1 and P-FZM-2 demand for high level regulations due to their activity concentrations higher than 1000Bq/kg (fig. 5-8). The application of the TENORMHARM classification system is connected with some difficulties, because both classification parameters are directly touched. The amount of affected people is only to be estimated roughly, in frame of the production process the number of persons might be less than 20, but maybe it will be exceeded during transportation and delivery. The quantity is also shaky, e.g. fertiliser are usually packed in 100kg bags, but a transportation truck takes up more than 20 tons. The result is on the one hand the category 2 "observation" or on the other category 3 "interventions must be undertaken". A proposal can be to classify the fertiliser for "to be observed" due to radionuclide concentrations lower than 1000Bq/kg, but "to carry out case studies" for the fused zirconia mullites because of their radionuclide concentrations of a few thousands Bq/kg.

6.1.5 Summary

The solid starting TENORM samples for the extraction procedures are by far mostly contaminated by natural radionuclides in such dimensions, that regulations according to national and international classification systems are obligatory. The repective type of intervention or monitoring action to be undertaken should be carried out with specific regard to the activity concentrations, amount of people might be affected and quantities of each substance as the examples of the fertiliser and fused zirconia mullites (see chapter "6.1.4 Products") show.

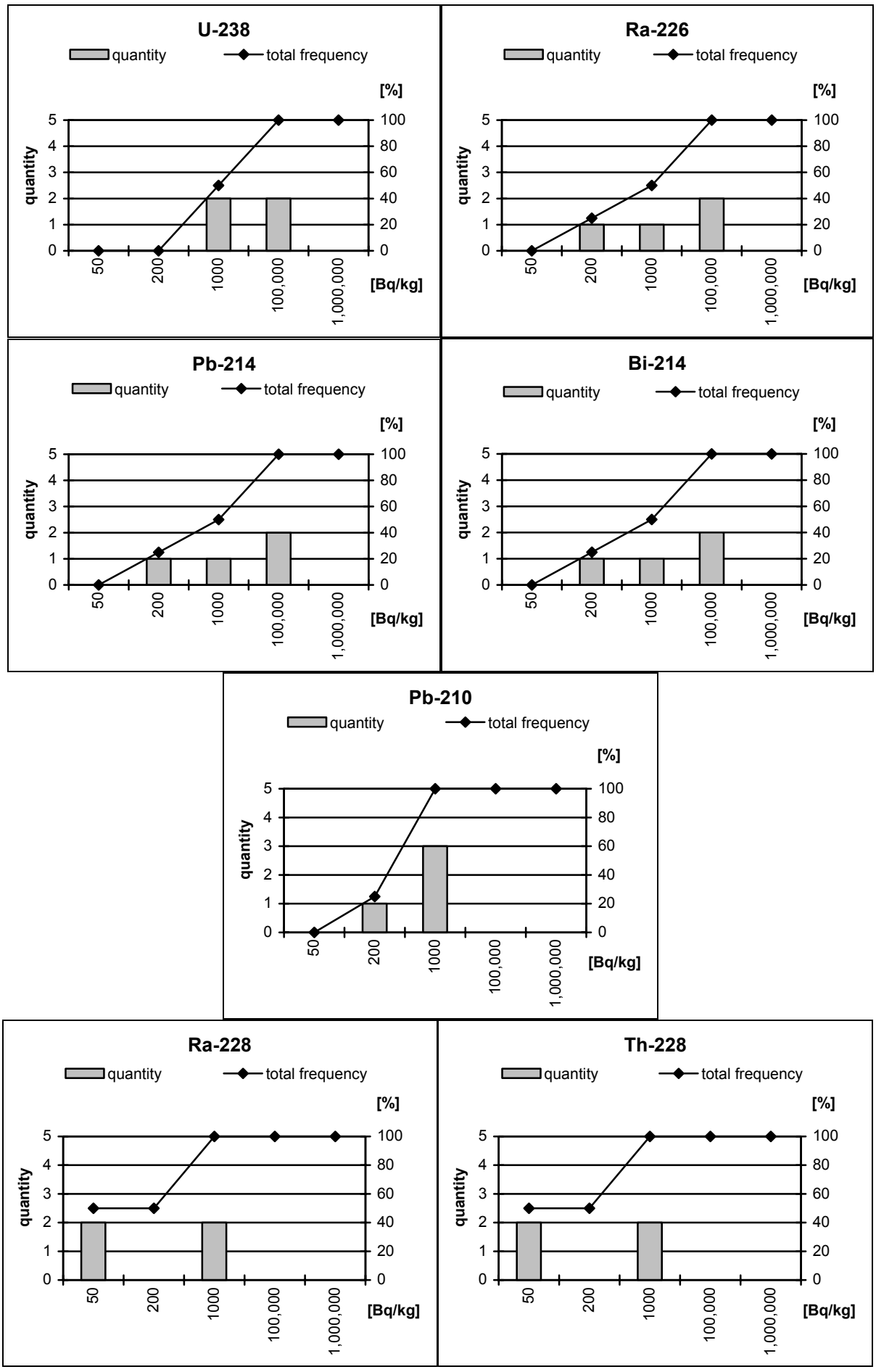

Fig. 6-4: Quantities and total frequencies of the 4 products classified by 5 activity concentration limits for each of the relevant radionuclides.

6.2 Radionuclide transfers

In general, the availability and chemical type of bounding of elements in solid materials is commonly investigated by the application of extraction procedures, mostly in sequential steps. The development of a 5-step procedure was established by TESSIER et al. in 1979 and since then, a number of only slightly different procedures have been developed. In order to ensure comparability of results, the European "Bureau Communautaire de Référence" (BCR) has proposed a standardised 3-step-method (URE et al., 1993). Sequential extraction procedures were originally developed for the determination of heavy metals, which is still commonly analysed for by ICP-AES. In relation to radiochemical aspects, thorium can be detected by ICP-AES, whereas ICP-MS has to be used for reliable uranium concentration determinations (MARTIN et al, 1998). SCHMIDT & WIEGAND (2003) investigated extraction solutions for their ^{226}Ra content by determining its progeny radon after equilibrium was reached. AGUADO et al. (2004) analysed extraction liquids for ^{226}Ra by alpha-spectrometry after treating the aliquot radiochemically to isolate the radium. LEOPOLD et al. (2007) verified the availability of radium isotopes and heavy metals as well from scales and tailings resulting from Polish hard coal mining by the application of the BCR-procedure and measuring the extractants by gamma-spectrometer.

In the following, the radionuclide transfers from the initial raw materials, possible pathways into waste or unwanted by-products and final products are presented. The radionuclides ^{214}Pb and ^{214}Bi are excluded due to their marked affinity to its precursor ^{226}Ra caused by the measurement procedure of awaiting equilibrium between them. In case of samples from one production site covering the whole manufacturing process radionuclide balances from the raw materials into wastes and products are enabled by the calculation of transfer factors.

6.2.1 Phosphate industry

The raw materials for the fertiliser industry are quite different in their radionuclide concentrations as shown in fig. 5-1. The determined activity concentrations for the Kola phosphate ore and the Moroccan as well are in well accordance to dimensions given by MARTIN et al. (1997) or PENFOLD et al. (1999). All the investigated materials came from only one industry site, which enables reliable transfer calculations for all relevant radionuclides (fig. 6-5). Due to the huge concentration differences between the raw materials R-PO-1 and R-PO-2, the radionuclide transfer is separated by both starting materials. For the Kola phosphate ore, the stream into the phosphogypsum waste means an enhancement by 2 for ^{238}U, by 1.35 for ^{226}Ra and by 2.76 for ^{210}Pb, whereas ^{228}Ra and ^{228}Th are slightly depleted. The radionuclide concentrations of the final fertiliser products are taken by average due to very similar activity concentrations. They are characterised by high uranium concentrations as also mentioned by PENFOLD et al (1999), which results in an enhancement factor of more than 40 for the Kola ore, ^{226}Ra and ^{210}Pb are enhanced by almost 7 and 14 respectively. The transfer factors of the Moroccan phosphate ore are the opposite: uranium, ^{226}Ra and ^{210}Pb are strongly depleted in both the phosphogypsum and the fertilisers as well, whereas the ^{232}Th progenies are slightly concentrated in the waste, but depleted in the fertiliser.

	raw material		waste material		final product	
	R-PO-1 (Kola)	TF	W-PG-1	TF	P-F-1 (NPK-type)	P-F-2 (PK-type)
		→		→ average		
	[Bq/kg]		[Bq/kg]		[Bq/kg]	[Bq/kg]
^{238}U	19.3	**2.08**	40.2	**44**	842	846
^{226}Ra	30.5	**1.35**	41.1	**6.95**	149	275
^{210}Pb	14.9	**2.76**	41.1	**14.5**	164	268
^{228}Ra	80.4	**0.75**	60.4	**0.18**	14.2	<11.1
^{228}Th	86.4	**0.57**	49.5	**0.08**	6.9	<6.9
	R-PO-2 (Morocco)					
^{238}U	1484	**0.03**	40.2	**0.57**	842	846
^{226}Ra	1479	**0.03**	41.1	**0.29**	149	275
^{210}Pb	1603	**0.025**	41.1	**0.27**	164	268
^{228}Ra	17.5	**3.45**	60.4	**0.81**	14.2	<11.1
^{228}Th	15	**3.3**	49.5	**0.46**	6.9	<6.9

Fig. 6-5: Radionuclide transfers from the raw materials R-PO-1 and R-PO-2 into the phosphogypsum waste W-PG-1 and the average of both fertiliser products P-F-1 and P-F-2 [TF: transfer factor].

The transfer factors into phosphogypsum can also be much higher for other fertiliser plants caused by higher radionuclide concentrations in that type of waste. AGUADO et al. (2004) report concentrations of 700-1000Bq/kg of ^{226}Ra for the phosphogypsum stockpiles of the Spanish Huelva fertiliser plants.

For the production process a mixing of both the phosphate ores can be assumed, because there is almost no difference in the radionuclide concentrations for both fertiliser types. The most important radionuclide transfer concerns uranium, which is set from the raw material towards the product due to uranium fixing of the phosphoric acid during the wet process, waste material is not affected. This circumstance comes along with a certain dilution as the transfer factors show and is also observed by RADULESCU & POPESCU (2002a). The very most of the initial radium concentration is removed from the production process by discharging waste water as shown by high concentrations (up to 14,000Bq/kg for ^{226}Ra) in sediments along sewers or rivers (POFFIJN & DE CLERK, 2004).

The absolutely extracted radionuclide concentrations of all the phosphate samples are presented in fig. 6-6. ^{226}Ra is that radionuclide being most frequently leached despite some ^{238}U and ^{210}Pb in case of P-F-2. R-PO-2 and the phosphogypsum waste W-PG-1 do not provide any mentionable amounts of radionuclides due to their poor initial radionuclide content. Also SILVA et al. (2002) observed very poor availabilities of ^{226}Ra, ^{210}Pb and ^{228}Ra from Brazilian phosphogypsum. The PK-fertiliser (P-F-2) leads to more totally leached radionuclides and also in higher dimensions in comparison with the NPK-type. It seems the nitrogen influences the radionuclides towards a stronger fixing, because the initial radionuclide concentrations are quite similar. The most important radionuclide in frame of the fertiliser production is ^{226}Ra, because it is present in all solid starting materials and also most frequently leached. Therefore, in fig. 6-7 the

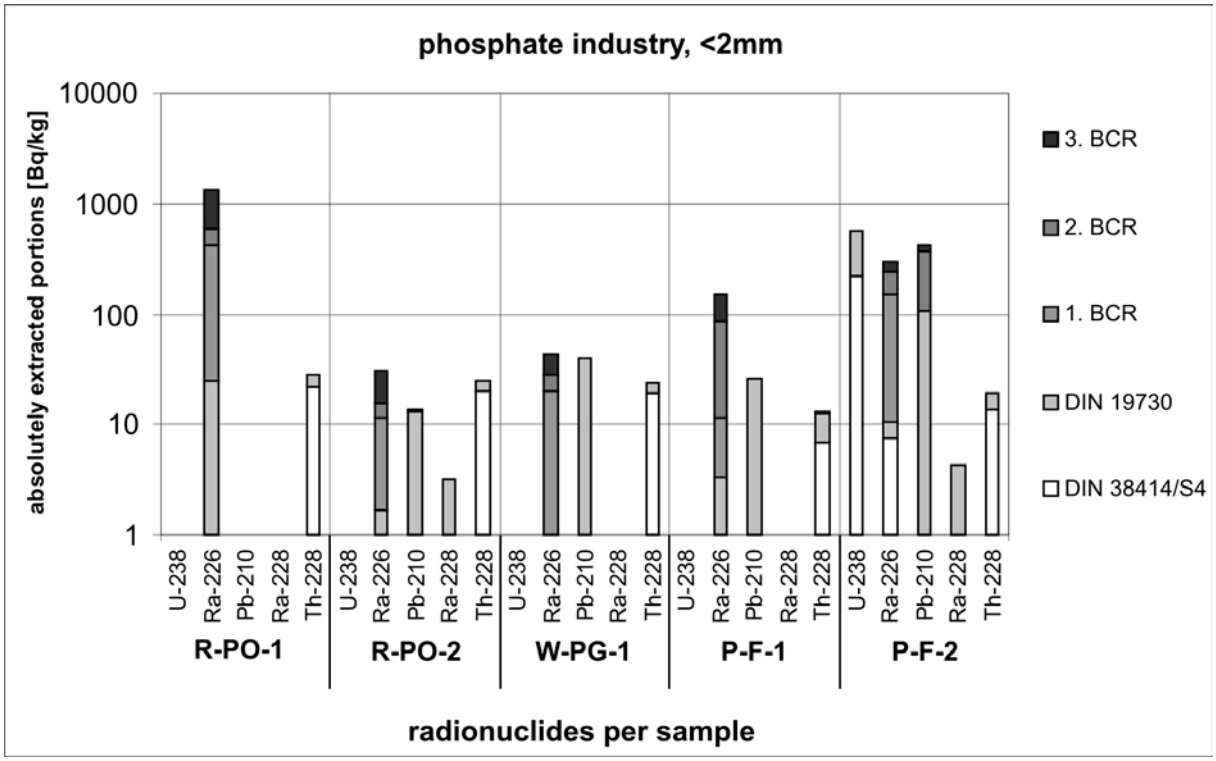

Fig. 6-6: Absolutely extracted radionuclide portions of all the phosphate samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

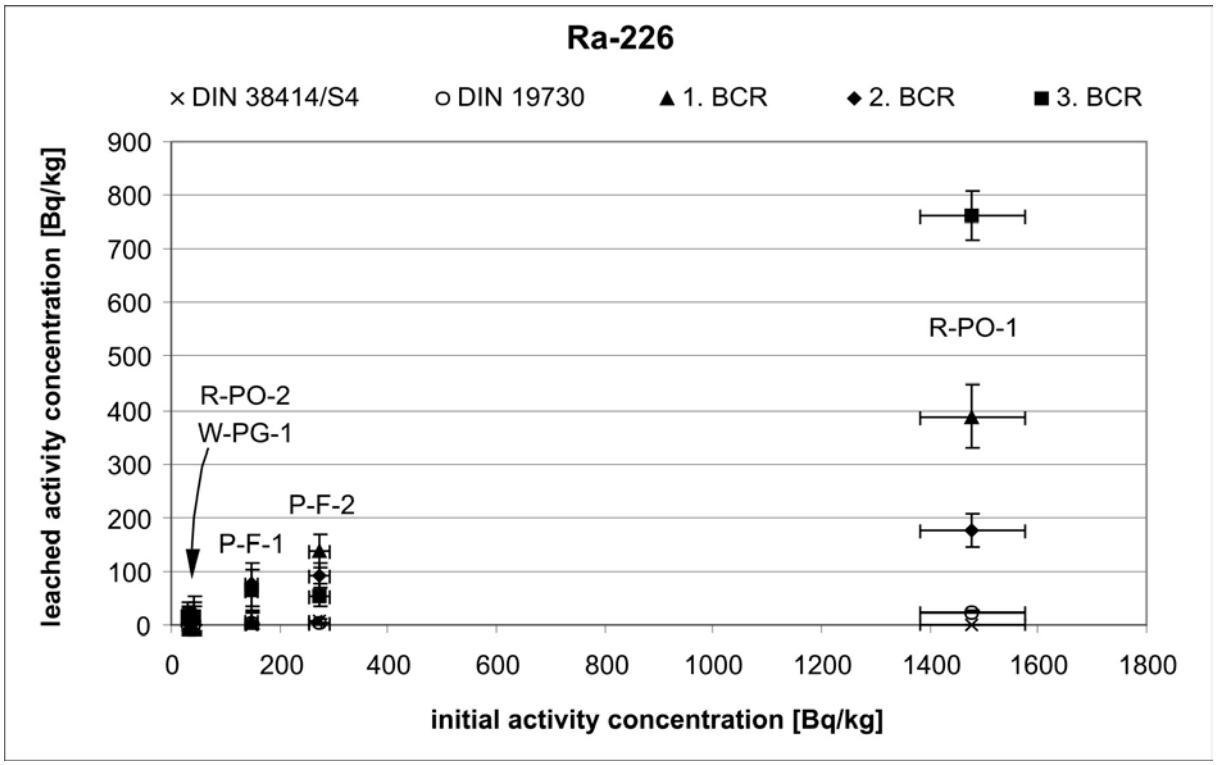

Fig. 6-7: Correlation of the ^{226}Ra specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

specific activities contained in the initial solid materials are correlated with the leached amounts. The Moroccan phosphate ore is of sedimentary origin and that is also indicated by the ^{226}Ra's leaching behaviour. Sedimentary phosphates are usually formed by the enrichment of phosphor

caused by small animals such as phytoplancton or animal particles (RICHTER, 1992). The by far most (50% of the initial content) of the radium is also bound in the oxidisable fraction representing organic matter and sulphides. The radium of the easily exchangeable fraction is weakly bound to grain surfaces. Especially the product P-F-2 underlines the fertilisers' water and plant providing characteristics. Radium is mostly bound in the easily exchangeable fraction and in addition, uranium and lead are present in the water soluble, plant available and easily exchangeable fractions as well (fig. 6-6).

6.2.2 Aluminium industry

The bauxite raw materials show significant differences in their radionuclide contents, but both are characterised by a maximum of lead activity concentrations (fig. 5-4). A main component of bauxites are silicates, which can contain some mentionable amounts of ^{210}Pb as reported by LOWE LEO (1992). That can be explained by similar chemical properties of silicium and lead, both are in the same group of chemical elements. The measured radionuclide concentrations of both bauxite samples and the red sludge waste as well are in very good agreement with those mentioned by GEORGESCU et al. (2005), who also investigated exactly the same substances. Since all materials are exclusively derived from the Romanian production site Tulcea, a reliable radionuclide transfer calculation is enabled. Due to huge variations in the concentrations of the uranium decay series' radionuclides, the transfer factors are separately determined for both starting materials (fig. 6-8). Despite the gentle enhancement of uranium from R-AO-1, all other radionuclides of the uranium decay series are reduced, in case of R-AO-2 an immense depletion of less than 0.1 can be observed. In contrast, the ^{232}Th progenies are concentrated by a factor of 3 roughly in both cases.

	raw material		**waste material**
	R-AO-1 (Boke)		W-RS-1 (Tulcea)
		TF →	
	[Bq/kg]		[Bq/kg]
^{238}U	130	**1.47**	191
^{226}Ra	230	**0.85**	195
^{210}Pb	423	**0.77**	329
^{228}Ra	176	**2.93**	516
^{228}Th	156	**2.94**	459
	R-AO-2 (Trombeta)		
^{238}U	863	**0.22**	191
^{226}Ra	2182	**0.09**	195
^{210}Pb	3928	**0.08**	329
^{228}Ra	169	**3.05**	516
^{228}Th	147	**3.12**	459

Fig. 6-8: Radionuclide transfers from the raw materials R-AO-1 and R-AO-2 into the red sludge waste W-RS-1 [TF: transfer factor].

The radionuclide transfers in frame of the bauxite disintegration process by soda lye (fig. 3-3) result obviously in a general dilution of uranium radionuclides for the red sludge waste, whereas radionuclides of the thorium decay series become enriched. A mixture of both raw materials can be assumed, but the respective mixing ratio must be taken for varying, because a constant availability of both raw materials is not probable. A possible "storage medium" for the uranium radionuclides might be the used leaching liquid soda lye, which is completely recycled in frame of the production process, but radiological data are not available.

The absolutely extracted radionuclide fractions are summarised in fig. 6-9. The extraction procedures clearly show that especially the aluminium ores provide ^{226}Ra and ^{210}Pb in huge amounts, ^{228}Ra is leached only in small dimensions. ^{226}Ra is frequently present in easily available extraction fractions, ^{210}Pb is exclusively found in the reducible fraction, which is in well accordance to the assumption lead would accompany the silicates. The supposed mentionable leaching of radionuclides from the red sludge waste in chapter "5.1.2 Aluminium industry" can not be proven. Instead, only ^{226}Ra is found to be leachable, but a significant portion (almost 100Bq/kg) is removed by water. Therefore, that waste material demands for some protection activities for the tailing ponds to prohibit the uncontrolled transfer of ^{226}Ra by water into the environment. This becomes especially evident as it is reported by RADULESCU & POPESCU (2005) that the tailing pond is planned to be permanently covered with a water layer of minimum 10cm in order to limit the material spreading by wind turbulences due to the missing of plants and radon and thoron emissions as well.

As obvious from fig. 6-9, ^{226}Ra is the radionuclide of interest for the aluminium industry, because it is extracted from all materials. Therefore, in fig. 6-10 the specific initial ^{226}Ra activities of the materials are correlated with the leached amounts. By taking the Trombeta bauxite R-AO-2 with the highest initial and leached activity concentrations, it can be concluded that the radium is quite easily available for plants (DIN 19730) and also surface adsorbed on the grains (1. BCR fraction). These results involves the question if the plants prospering on the Brazilian Trombeta zone's bauxite are significantly contaminated by ^{226}Ra. Smaller amounts are proven to be available under reducing (2. BCR fraction) and oxidising conditions (3. BCR fraction). In relation to these activity concentrations those of both the other samples are quite small, but in case of the DIN 19730 and 1. BCR fraction same leaching behaviours, which means highest portions, are recognisable for the bauxite sample of the Boke zone (R-AO-1).

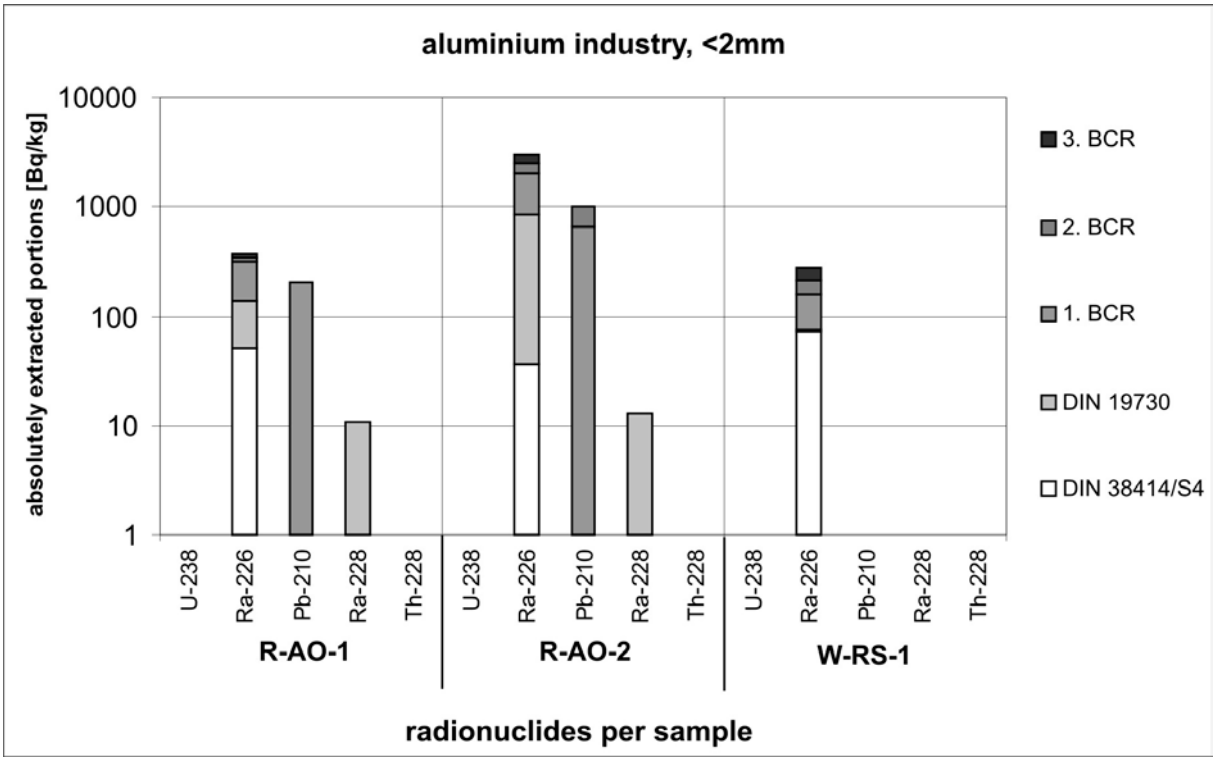

Fig. 6-9: Absolutely extracted radionuclide portions of all the aluminium samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

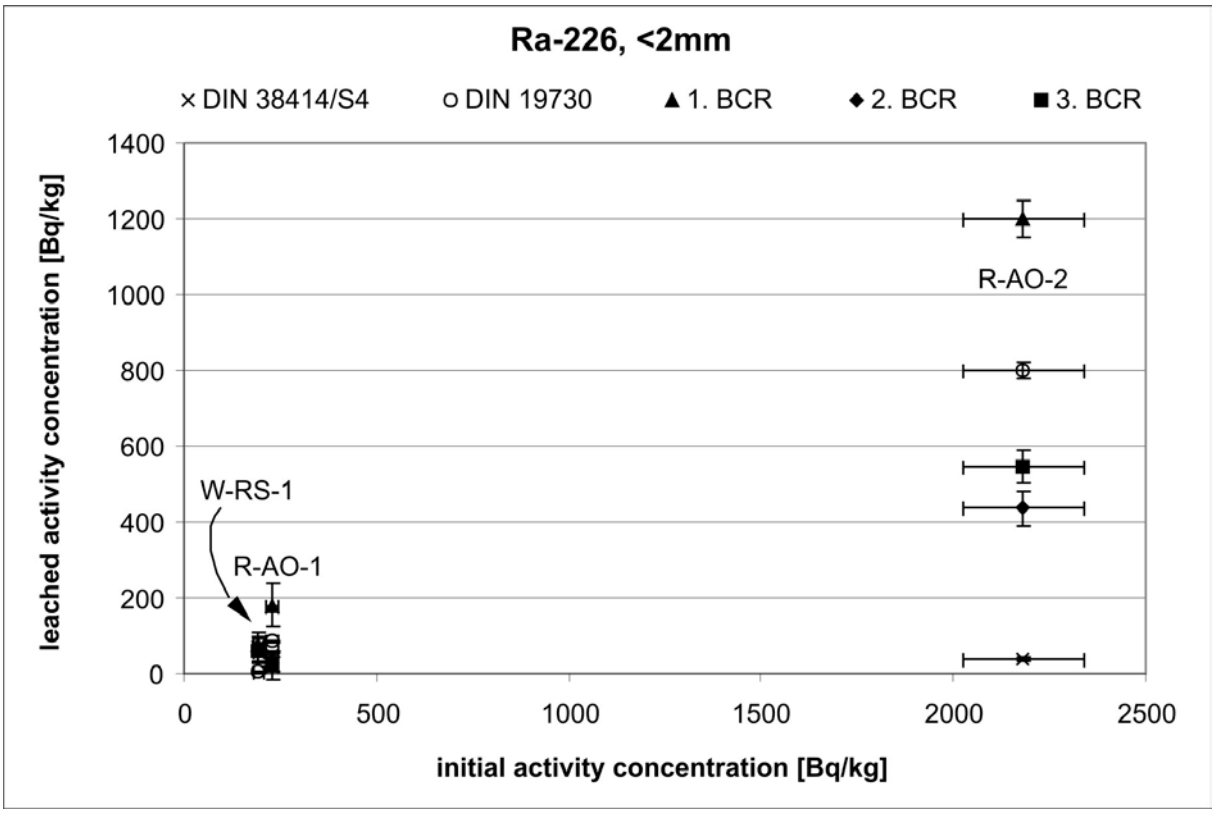

Fig. 6-10: Correlation of the ^{226}Ra specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

6.2.3 Refractory industry

The raw material zircon sand being used as an additive in frame of the refractory production shows enhanced activity concentrations especially for the uranium decay series, which is characteristic for the main component zirconium. The radionuclides of both decay series are present in equilibrium as to be expected for untreated substances of natural state and without a significant loss of volatiles. As mentioned in the chapter "2.2 Definitions of radioactive materials", in frame of the geological genesis called magmatic differentiation uranium/thorium can be relatively enriched in the magmatic fluid because they are incompatible elements due to their ion radius. Therefore, uranium and thorium are then fixed in the crystal lattice of late solidified minerals such as the heavy mineral zirconium (DYBEK, 1962). The immense heating in the electric arc furnace (fig. 3-5) leads then to an interruption of the uranium decay series, because temperatures of more than 2000°C volatilise ^{210}Pb and ^{210}Po, the latter is out of consideration in frame of this thesis. The resulting fume transfers ^{210}Pb into the dust filters as presented in fig. 6-11, the transfer factor is given by more than 60. The magnitude of the ^{210}Pb activity concentration is in good agreement with those generally reported for that type of filter (PENFOLD et al., 1999, ZAMPIERI et al., 2005). In contrast, all other relevant radionuclides are significantly depleted down to 10% roughly, because they are not affected by the fusion process as the lead is. The radionuclide concentrations in the final products seem to depend on the special kind of material. The fused zirconia mullite P-FZM-1 shows slightly depleted activity concentrations for all radionuclides the transfer factors ranging between 0.5 and 0.7, whereas P-FZM-2 is characterised by a smooth enhancement of 1.1 up to 1.5. Both substances have exactly the same, reduced to a third ^{210}Pb concentration compared with the raw material, which is explained by the lead transfer into the filter dust.

	raw material		**waste material**		**final product**
	R-ZS-1	**TF** →	W-FD-1	**TF** →	P-FZM-1
	[Bq/kg]		[Bq/kg]		[Bq/kg]
^{238}U	2575	**0.11**	289	**0.71**	1829
^{226}Ra	2930	**0.1**	295	**0.55**	1601
^{210}Pb	2610	**62.2**	162,400	**0.36**	932
^{228}Ra	762	**0.1**	74	**0.51**	388
^{228}Th	690	**0.12**	80	**0.54**	369
					P-FZM-2
				TF →	
^{238}U	2575			**1.52**	3913
^{226}Ra	2930			**1.44**	4206
^{210}Pb	2610			**0.36**	950
^{228}Ra	762			**1.12**	853
^{228}Th	690			**1.13**	780

Fig. 6-11: Radionuclide transfers from the raw material R-ZS-1 into the filter dust waste W-FD-1 and both the products P-FZM-1 and P-FZM-2 [TF: transfer factor].

All the radionuclides' leached activity concentrations are summarised in fig. 6-12. It is generally noticed that beside its extremely high initial ^{210}Pb activity concentration the filter dust sample W-FD-1 also provides the by far most of it in frame of the extraction procedures. A third which means 44,200Bq/kg is bound to sulphides (fig. 5-41), organic matter can be excluded. Another portion of 17,500Bq/kg is found in the reducible fraction beside 1100Bq/kg in the plant available fraction. That leads to the conclusion that the filter dust material is of heterogeneous composition so that the volatilised ^{210}Pb can be fixed on different chemical components. In the case of storing that type of material outside on a stockpile attention must be paid towards the pathway into plants. In contrast, ^{226}Ra is determined in all the materials extraction liquids in roughly same dimensions with a slight accentuation on the reducible fraction (2. BCR). ^{228}Th is also found in absolutely same magnitudes in the extractants of the water soluble and plant available fractions, but in very low amounts.

Since ^{226}Ra is present in many extraction liquids of all solid materials, it is correlated with the respective initial activity concentrations of the substances (fig. 6-13). As shown, the water soluble and plant available fractions from all materials do not contain mentionable amounts of leached radium. The raw material zircon sand provides ^{226}Ra under reducible and oxidisable conditions in almost same dimensions, which might be due to the fact that the precursor ^{238}U interspers the mineral zircon resulting in a radium binding to those elements as they are available in the crystal lattice. A slightly higher amount (150Bq/kg) is proven for the grain surface adsorbed portion, which underlines the assumption mentioned before. Also the filter dust W-FD-1 shows similar, relatively low radium leaching behaviours for all three BCR fractions without any predominating preference. This circumstance is a further support for the idea of a heterogeneous material composition. The final products are characterised by opposite leaching behaviours: on the one hand the sample P-FZM-1 provides the most radium under oxidisable conditions, on the other P-FZM-2 is determined for the highest radium portion to be fixed in the reducible fraction. In both cases, the surface adsorbed amount is of intermediate dimension. Due to these different extraction behaviours of the same kind of product, which can not be explained by the different grain sizes, reliable statements about the radium's dominating type of bounding in fused zirconia mullite are not enabled.

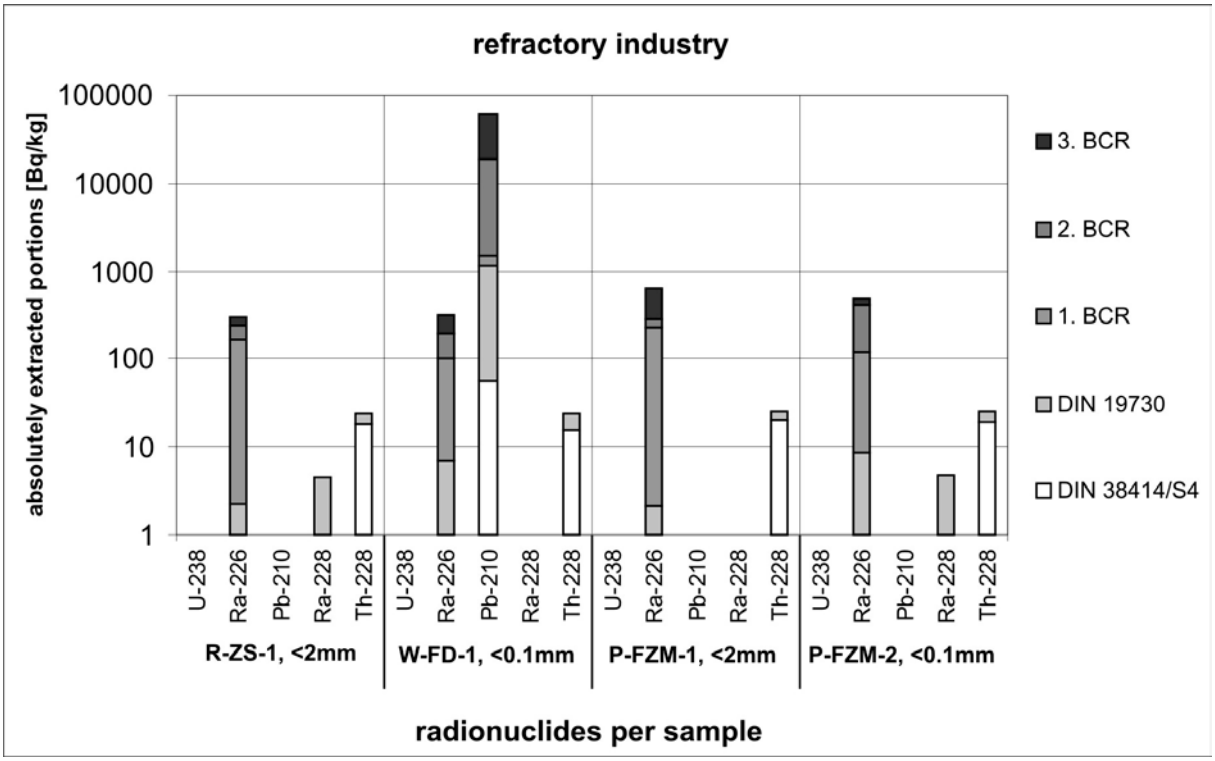

Fig. 6-12: Absolutely extracted radionuclide portions of all the refractory samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

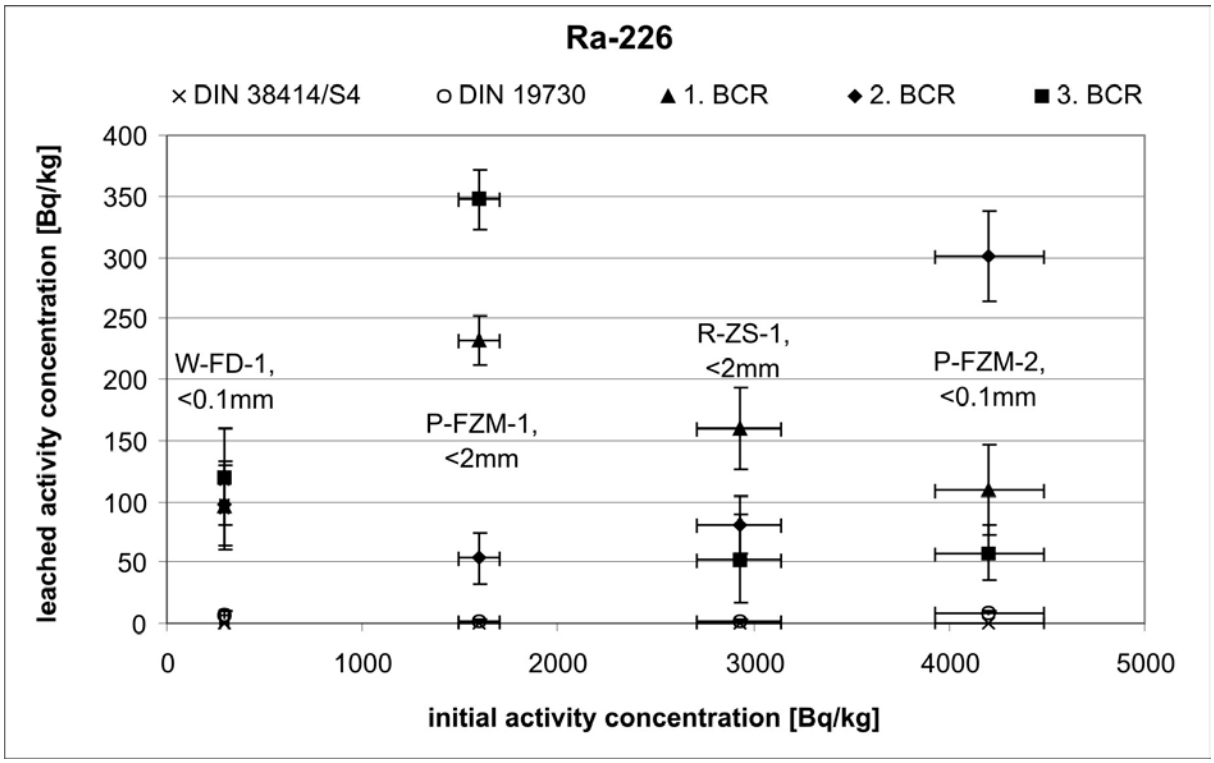

Fig. 6-13: Correlation of the ^{226}Ra specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

6.2.4 Crude oil exploitation

In frame of crude oil exploiting only waste materials such as sludge and scales are of radiological relevance and therefore delivered, so no radionuclide transfer calculations from raw materials like crude oil are possible.

Although the crude oil itself is reported to contain only rather low radionuclide concentrations (GODOY & PETINATTI DA CRUZ, 2003), the rock formations holding the crude oil can contain mentionable amounts of uranium and thorium and respective progenies in the rock matrix (HEATON, 1995), which are then brought to the surface by pumping the formation water upwards. The main pollutants of the waters are ^{226}Ra, ^{228}Ra and ^{210}Pb. The decreasing concentrations in installations especially of the radium isotopes are obviously correlated to increasing distances from the bore hole (HARTOG et al., 1998; SCHMIDT, 1998). This phenomenon is also proved by the investigated sludge and scale samples. The sludge mainly occurs in the direct vicinity of the bore hole as a remnant of the drilling process and contains huge activity concentrations of both ^{226}Ra and ^{228}Ra beside ^{210}Pb (fig. 5-9), whereas the scales are found in pipelines and tubes and are mainly contaminated by the unaffected ^{210}Pb (fig. 5-10) (see chapter "3.4.2 Produced TENORM").

The predominating position of the radium isotopes and ^{210}Pb in the sludge and scale samples is also obvious from their extracted portions (fig. 6-14). Uranium is not present in the initial samples, but all other relevant radionuclides are significantly leached by the applied procedures. ^{226}Ra and ^{228}Ra show almost comparable activity concentrations in the very most of the extraction

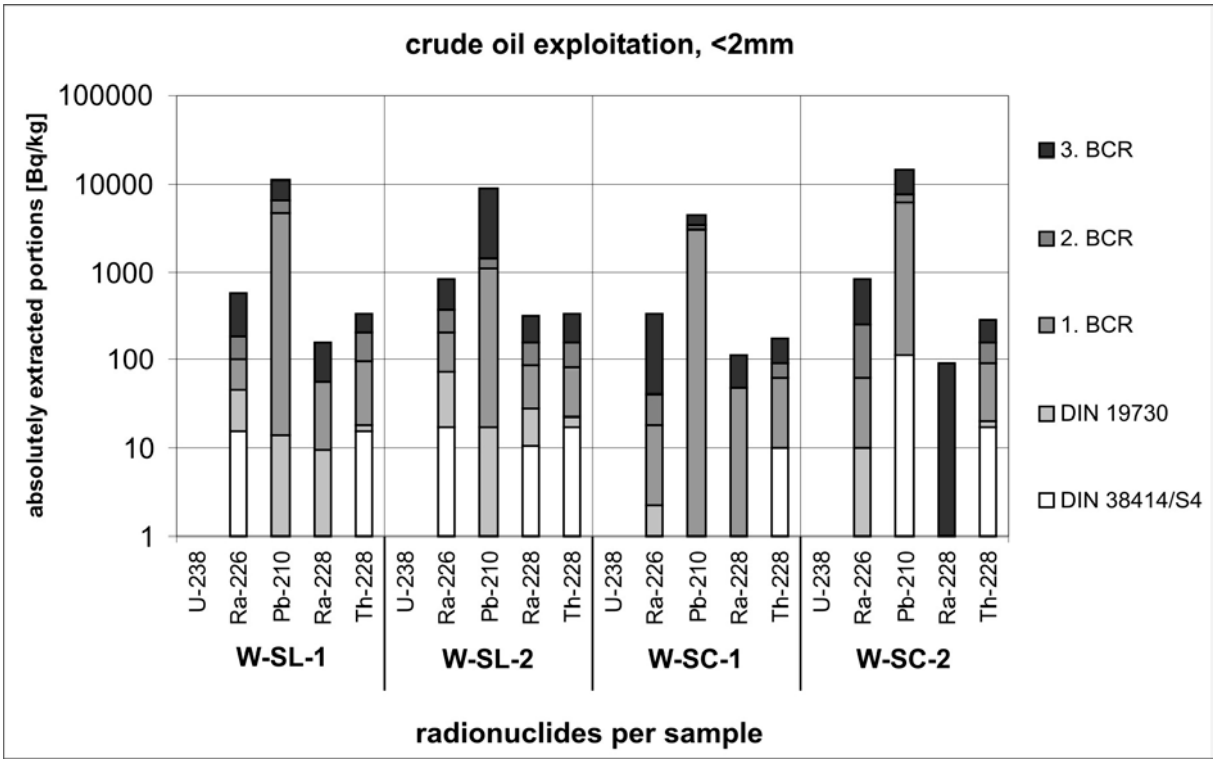

Fig. 6-14: Absolutely extracted radionuclide portions of all the crude oil exploitation samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

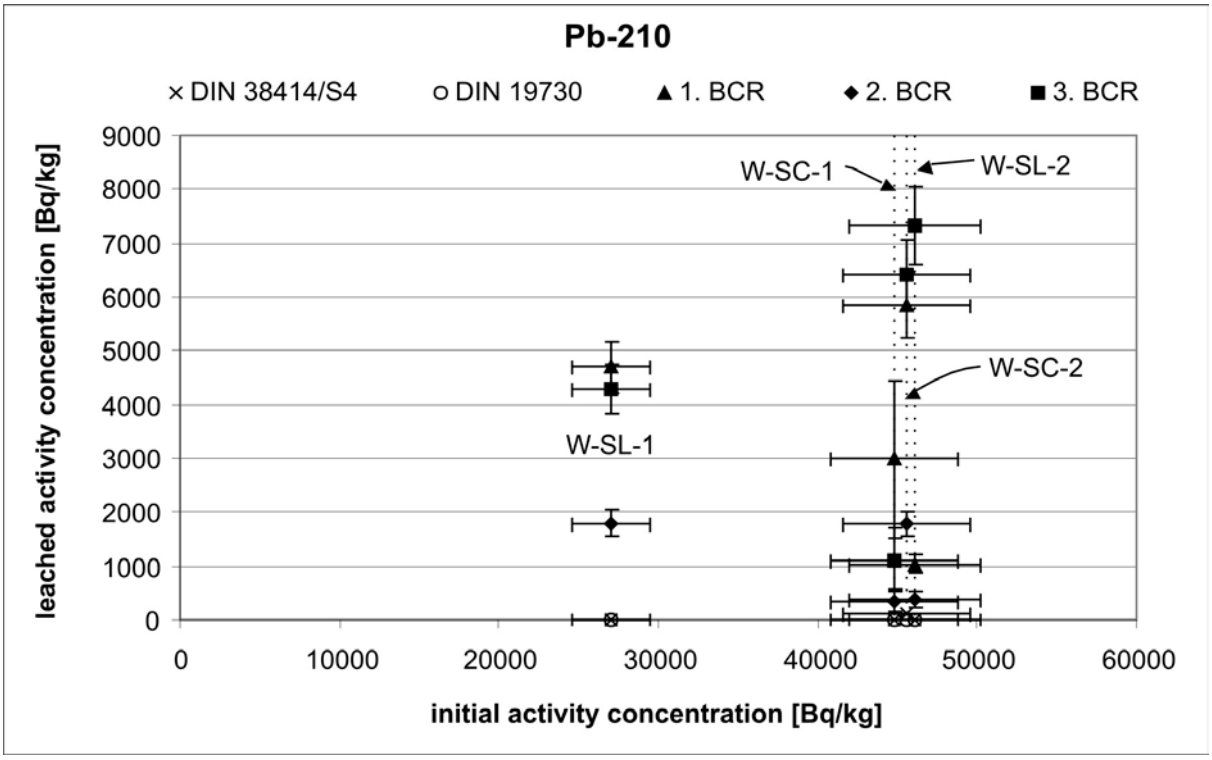

Fig. 6-15: Correlation of the ^{210}Pb specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

liquids, ^{228}Ra is mainly present in smaller dimensions than ^{226}Ra due to lower initial concentrations. One exemption is the scale W-SC-2, which provides ^{228}Ra exclusively under oxidising conditions. This might be caused by a huge portion of organo-sulphur components resulting from the crude oil. The progeny ^{228}Th is present in all the extractions in nearly same dimensions. The omnipresence of all the radionuclides in almost all extractants can be due to especially heterogeneous material compositions of the samples as a result of many different materials being tapped during drilling. But no doubt, ^{210}Pb is that radionuclide of relevance, which is therefore highlighted in fig. 6-15. As shown, lead is not mentionable determined in the water soluble and plant available fractions. The most of the ^{210}Pb is mainly present in the oxidisable fraction without a distinction between sludge or scale, which leads to the conclusion that lead is frequently bound as PbS being typical for such reducing milieus as organic substances establish. Another important fraction is the grain surface adsorbed one, the portion of iron and manganese oxides steps back significantly. In summary, the lead's leaching behaviour and also the dimensions of the leached activity concentrations show no evident differences between the materials, i.e. if it's sludge or scale.

6.2.5 Hard coal extraction

From the hard coal extraction process, only the unwanted by-products sediments are available, so no radionuclide tranfer calculations can be undertaken. In addition due to small sample volumes, only the BCR extraction scheme is enabled. The common feature for all the obtained liquids is that despite ^{228}Th and ^{226}Ra in one case no other radionuclide was leached

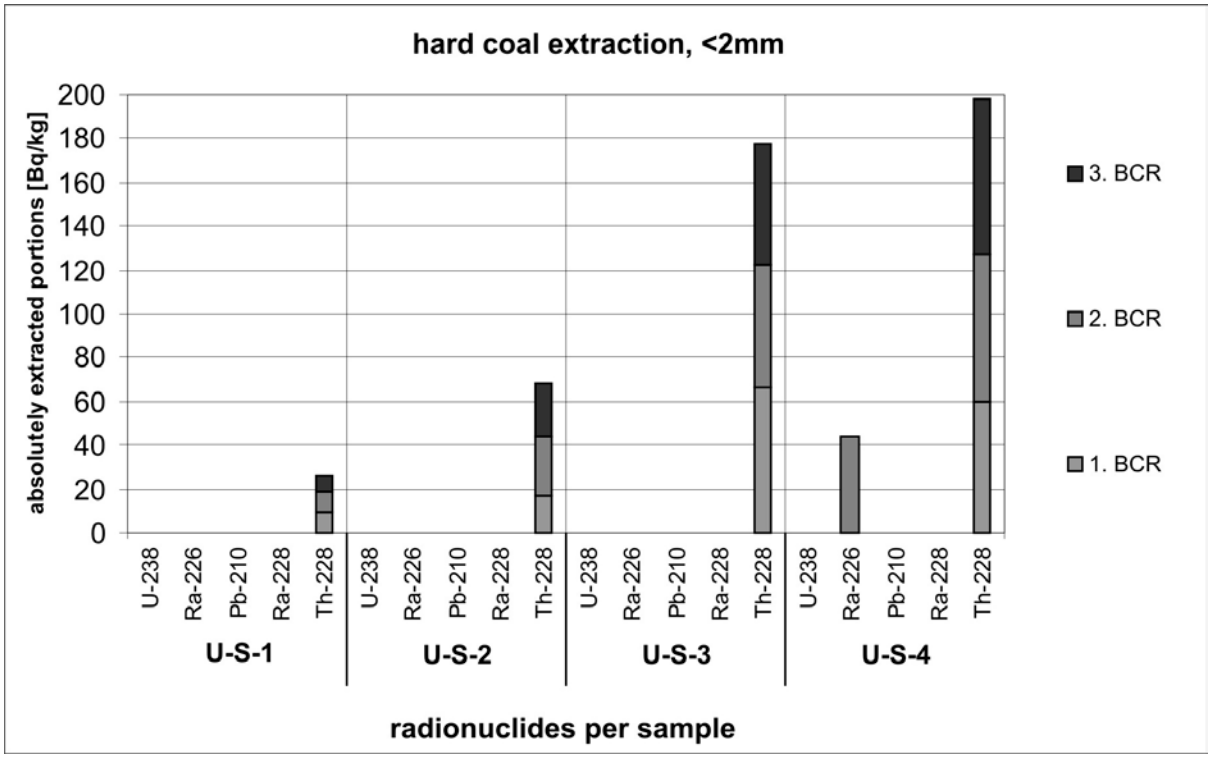

Fig. 6-16: Absolutely extracted radionuclide portions of all the hard coal extraction's samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

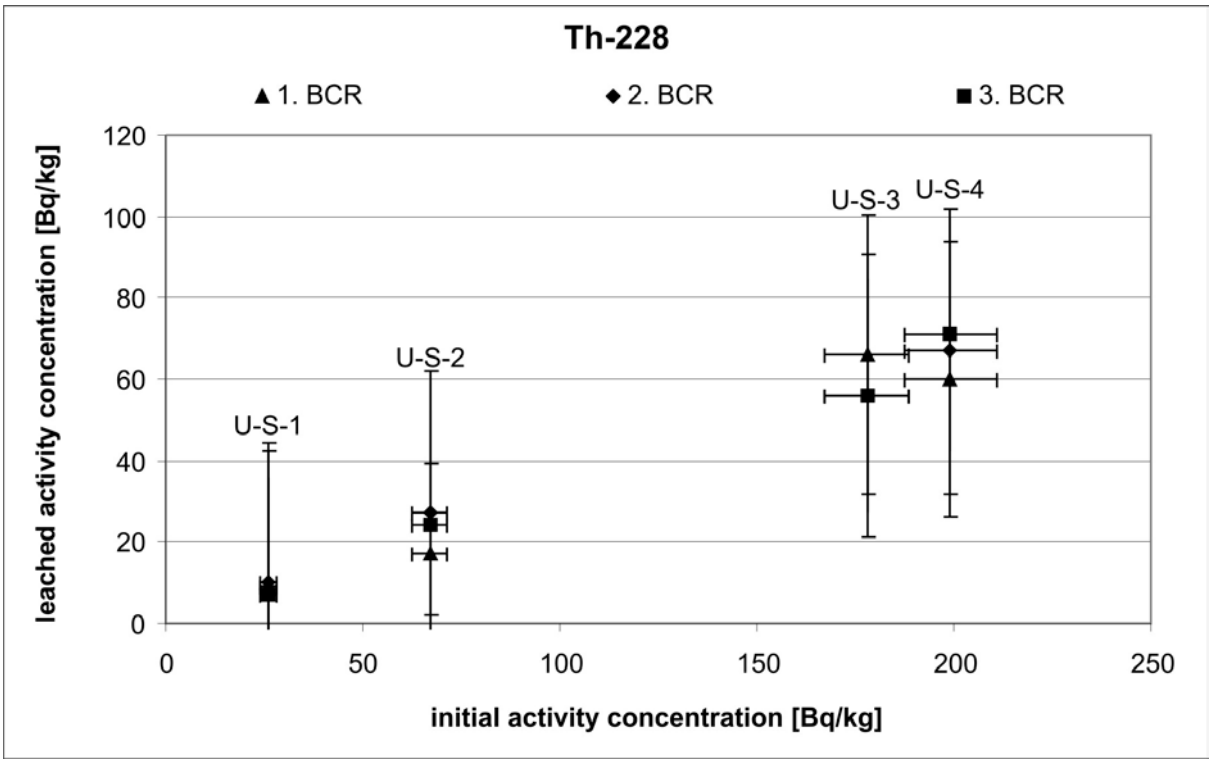

Fig. 6-17: Correlation of the ^{228}Th specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

(fig. 6-16). It is remarkable that ^{228}Th is present in all the fractions by almost same portions and the higher the initial activity concentrations the higher the leached amounts, which leads to the conclusion that there is no preferred type of bounding for ^{228}Th as shown in fig. 6-17. Up to now,

only the radium isotopes were in the focus of leaching investigations of materials from hard coal mining (SCHMIDT & WIEGAND, 2003, CHALUPNIK & AGUADO, 2005). Whereas all the other radionuclides are not detected in any of the BCR extractants despite ^{226}Ra in the 2. BCR fraction of sample U-S-4, ^{228}Th is always leached. Its precursor ^{228}Ra can also be taken for being strongly fixed in the radiobarite's crystal lattice as it is known from ^{226}Ra (SCHMIDT, 2001), it is never extracted. Also LEOPOLD et al. (2007) observed almost all the radium remaining in the BCR residuals, if radiobarite acts as a radium carrier. Therefore, ^{228}Th is the point where the thorium decay series gets interrupted and mobilised under reducible and oxidisable conditions and from grain surfaces as well. This is to be highlighted the more as the radionuclide concentrations of the thorium decay series reported in literature (table 3-6) usually step back those of the uranium decay series. But the leached amounts of ^{228}Th are only considerable, if the activity concentrations of the precursor ^{228}Ra are also mentionably enhanced by exceeding 1000Bq/kg roughly, otherwise the mobilisable thorium is too small for an environmental hazard potential.

6.2.6 Thorium compounds industry

Since all the materials from thorium processing industries are to be classified as unwanted by-products and the substances they are resulting from are not available anymore, transfer calculations are not enabled. Apart from sample U-SO-4, all the soils contain strongly enhanced initial activity concentrations of all relevant radionuclides including those of the uranium decay series (5-12). The applied leaching methods lead to significant amounts of extracted radionuclide concentrations, too (6-18). The water solubility is reduced for all radionuclides. The soil

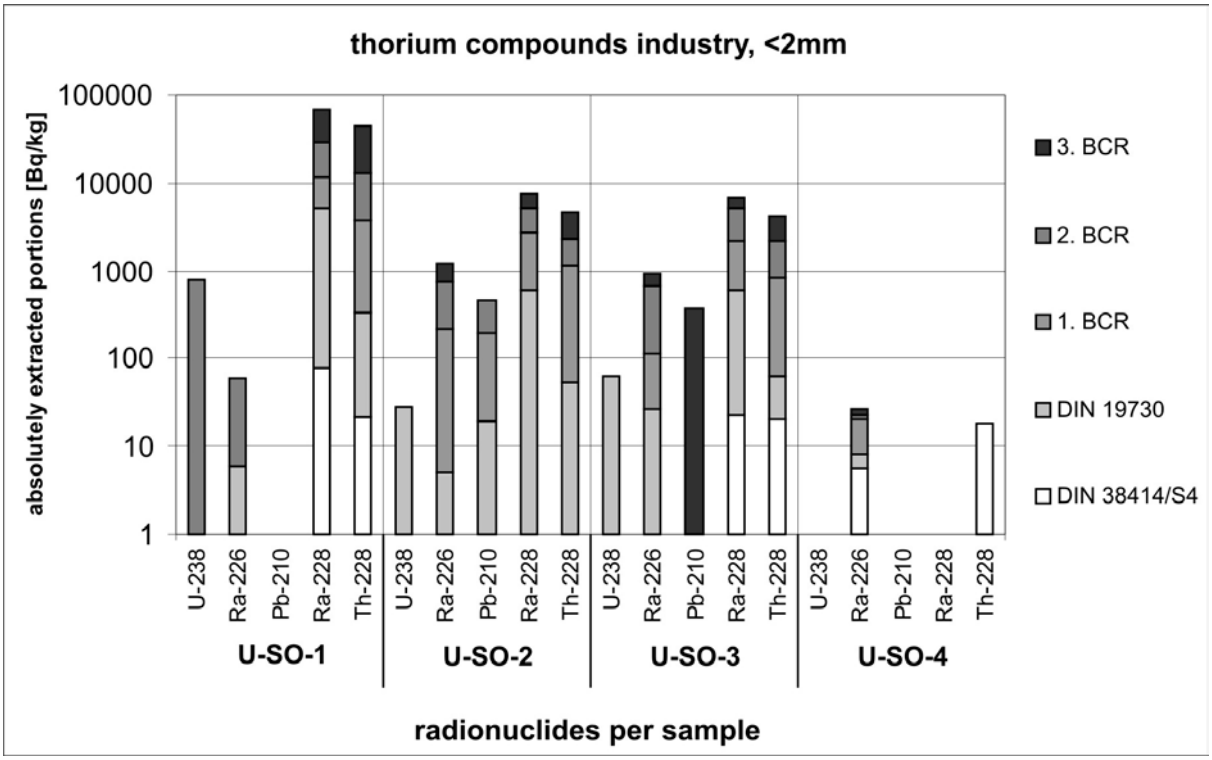

Fig. 6-18: Absolutely extracted radionuclide portions of all the thorium compounds samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

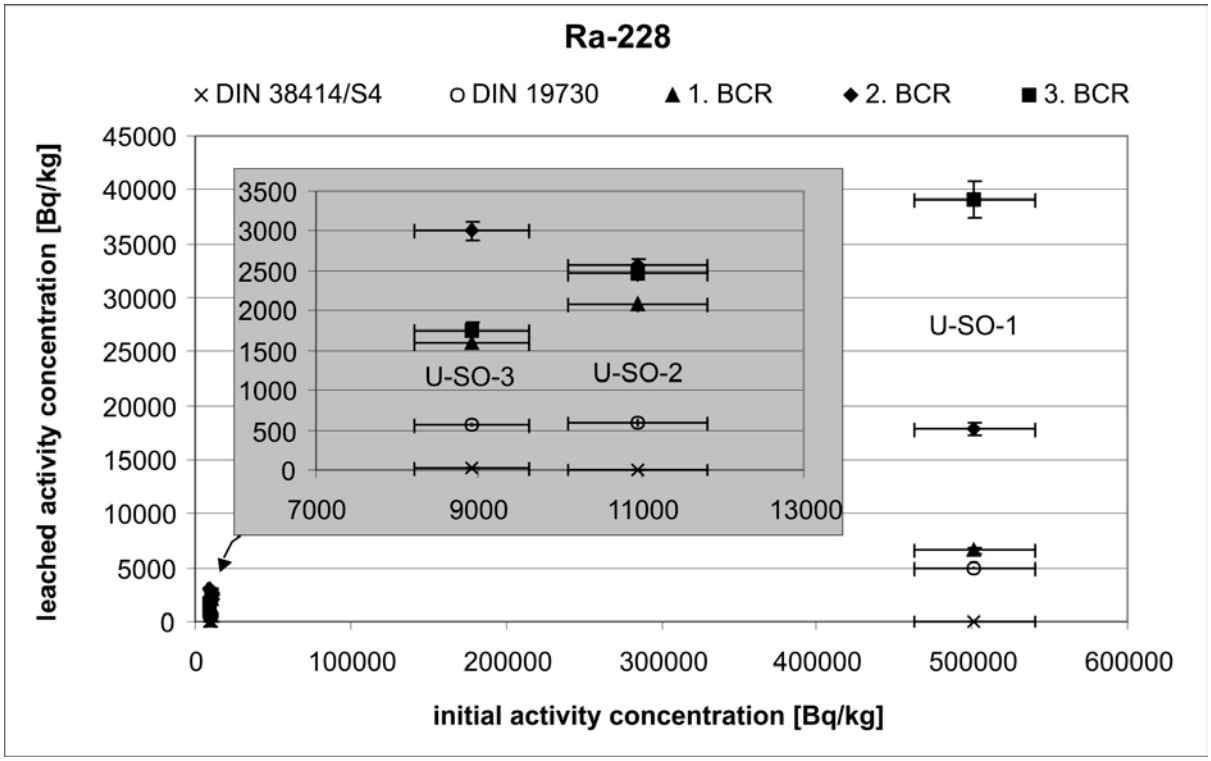

Fig. 6-19: Correlation of the ^{228}Ra specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

containing residues of the thorium-cobalt catalysts (U-SO-1) also provides uranium, which is exclusively found in the reducible fraction (2. BCR), so it got dissoluted from some uranium oxides. The residues of the FISCHER-TROPSCH synthesis (U-SO-2 and U-SO-3) contain few amounts of plant available uranium. The sample U-SO-3 contained lead leachable by the 3. BCR step, which identifies its chemical type of bounding as sulphidic and PbS can be assumed for the main component. In contrast, sample U-SO-2 shows opposite characteristics: ^{210}Pb is only found in the easily available fractions (plant available and grain surface adsorbed) beside some being bound to oxides. The ^{232}Th progenies are present in all the soils' BCR extraction liquids apart from U-SO-4, which can be explained by the heterogeneous compositions of the soil samples consisting of oxides and sulphides/organic matter as well, so the immense activity concentrations are distributed among all investigated types of bounding due to sheer presence.

Since ^{228}Ra shows the highest amounts of extracted portions, it is taken as a representant and the leached amounts are correlated versus the initial activity concentrations in fig. 6-19. It is once again visible that nothing is leached by water, but the radium's plant availability is proven for all samples in significant dimensions. The grain surface adsorbed portions are lower than both the other BCR fractions in all cases. A difference between the catalyst residue (U-SO-1) and the FISCHER-TROPSCH residues (U-SO-2 and U-SO-3) is that the by far most of ^{228}Ra is bound to sulphides and organic matter in case of the first mentioned sample, whereas U-SO-3 provides it in highest volumes under oxidisable conditions. U-SO-2 does not really show distinctions between the reducible and oxidisable portions. The differences in the types of bounding might be due to changes of the mineral compositions in each of the soils.

6.2.7 Uranium industry

The uranium bearing hard rocks used as raw materials and the produced tailing wastes come from the same production site Gorenja Vas located in Slovenia, therefore radionuclide transfers can be reliably calculated and are presented in fig. 6-20. The raw materials R-UO-1 and R-UO-2 are characterised by an evident difference between their initial radionuclide concentrations, those of R-UO-2 are roughly enhanced by a concentration factor of 7 in comparison with R-UO-1 being due to natural variations in the hard rocks radionuclide concentrations. But apart from that, all the uranium radionuclides are strongly depleted in the tailings. In relation to sample R-UO-1, the transfer factors are mostly much lower than 10%, in case of R-UO-2 they even range in pars pro mille with a maximum of 20‰. All the calculated transfer factors also reflect the correlations between the ^{238}U, ^{226}Ra and ^{210}Pb activity concentrations given in table 5-1. The phenomenon of

	raw material				**waste material**
	R-UO-1	**TF**	W-T-1	**TF**	W-T-2
	[Bq/kg]		[Bq/kg]		[Bq/kg]
^{238}U	130,900	**0.01**	1553	**0.01**	1875
^{226}Ra	94,215	**0.05**	4691	**0.06**	5556
^{210}Pb	123,420	**0.07**	9189	**0.08**	10,260
^{228}Ra	n.d.		31.2		28.7
^{228}Th	n.d.		32.4		27.3
			W-T-3		W-T-4
^{238}U	130,900		n.d.	**0.01**	1773
^{226}Ra	94,215	**0.1**	9754	**0.03**	3010
^{210}Pb	123,420	**0.13**	15,910	**0.06**	7844
^{228}Ra	n.d.		32.7		28.1
^{228}Th	n.d.		30.9		29.7
	R-UO-2	**TF**	W-T-1	**TF**	W-T-2
	[Bq/kg]		[Bq/kg]		[Bq/kg]
^{238}U	832,580	**0.002**	1553	**0.002**	1875
^{226}Ra	894,650	**0.005**	4691	**0.006**	5556
^{210}Pb	856,000	**0.01**	9189	**0.012**	10,260
^{228}Ra	n.d.		31.2		28.7
^{228}Th	n.d.		32.4		27.3
			W-T-3		W-T-4
^{238}U	832,580		n.d.	**0.002**	1773
^{226}Ra	894,650	**0.011**	9754	**0.003**	3010
^{210}Pb	856,000	**0.019**	15,910	**0.009**	7844
^{228}Ra	n.d.		32.7		28.1
^{228}Th	n.d.		30.9		29.7

Fig. 6-20: Radionuclide transfers from the raw materials R-UO-1 and R-UO-2 into the tailings W-T-1, W-T-2, W-T-3 and W-T-4 [TF: transfer factor, n.d.: not detected].

higher dimensions the farther the uranium progenies are positioned in the decay series is also observed by MOFFETT (1977) and KRIZMAN et al. (1995), the latter investigated exactly the Zirovski vrh mine's tailings. They report strong unbalanced radionuclide ratios as described for ^{230}Th (4000Bq/kg) and ^{226}Ra (8000Bq/kg), which are in good agreement with the measured ones presented in this thesis, and attribute them to some co-leaching of uranium's next progenies in frame of the extraction process. This is also the explanation given by MOFFETT (1977).

MERKEL & DUDEL (1998) investigated tailings of the former uranium mining site Schneckenstein, which is located in the German area called Vogtland. They proved the tailings to contain ^{230}Th, ^{226}Ra and ^{210}Pb in almost same concentrations in the range of 4000-6000Bq/kg, uranium is reported to be depleted by an average factor of 0.4 in comparison with its progenies. Due to that relatively high depletion factor the authors concluded that the uranium extraction was not of really satisfying quality, a considerable portion of the initial uranium content (40%) is said to have remained in the tailings. In case of the Slovenian tailings, the calculations can not be applied in that way as described by MERKEL & DUDEL (1998), because the uranium progenies are not present in equilibrium. For sure, the transfer factors presented in fig. 6-20 are calculated for idealised conditions, e.g. the raw materials are characterised by a wide spread of the radionuclides concentrations and are considered for a 100% portion without any dead rock impurities. This was not the fact during the uranium production process, but nevertheless higher extraction rates and therefore better quality can be assumed in view of the extremely low transfer factors.

All the materials' absolutely extracted amounts are presented in fig. 6-21. All the uranium decay series' radionuclides of the sandstones R-UO-1 and R-UO-2 are equally distributed among the BCR fractions, which means there is no preferred type of bounding, so the uranium is not only bound in frequent oxides such as uraninite [UO_2], uranium trioxide [UO_3] or triuranium octaoxide [U_3O_8], but also huge organic matter and grain surface adsorbed portions occur. In comparison, both the slags U-ST-1 and U-ST-2 provide only really low radionuclide amounts, but the most of them are water available. The pegmatite U-ST-3 is significantly different from the sandstones, a huge portion of ^{238}U and ^{226}Ra and all of ^{210}Pb are fixed in the oxidisable fraction, so sulphides such as PbS are the main carriers. This is also valid for the breccia U-ST-4, but in bigger dimensions. Especially for the latter the result is surprising, because on the rock's surface pitchblende spheroids were clearly identified (see appendix, chapter "A-1 Material descriptions"). So that uranium mineral and perhaps also other uranium oxides as mentioned above might not be leached in those dimensions by the 2. BCR fraction "bound to iron and manganese oxides" as to be expected. Another hint is the uranium's leaching behaviour of the samples R-UO-1 and R-UO-2, they do not show a clearly preferred oxidic fixing of uranium as one can suppose. If these assumptions would be proven true, it means a limitation of the BCR extraction procedure's applicability for leaching radionuclides (see chapter "6.2.8 Judgement of the extraction prodecures").

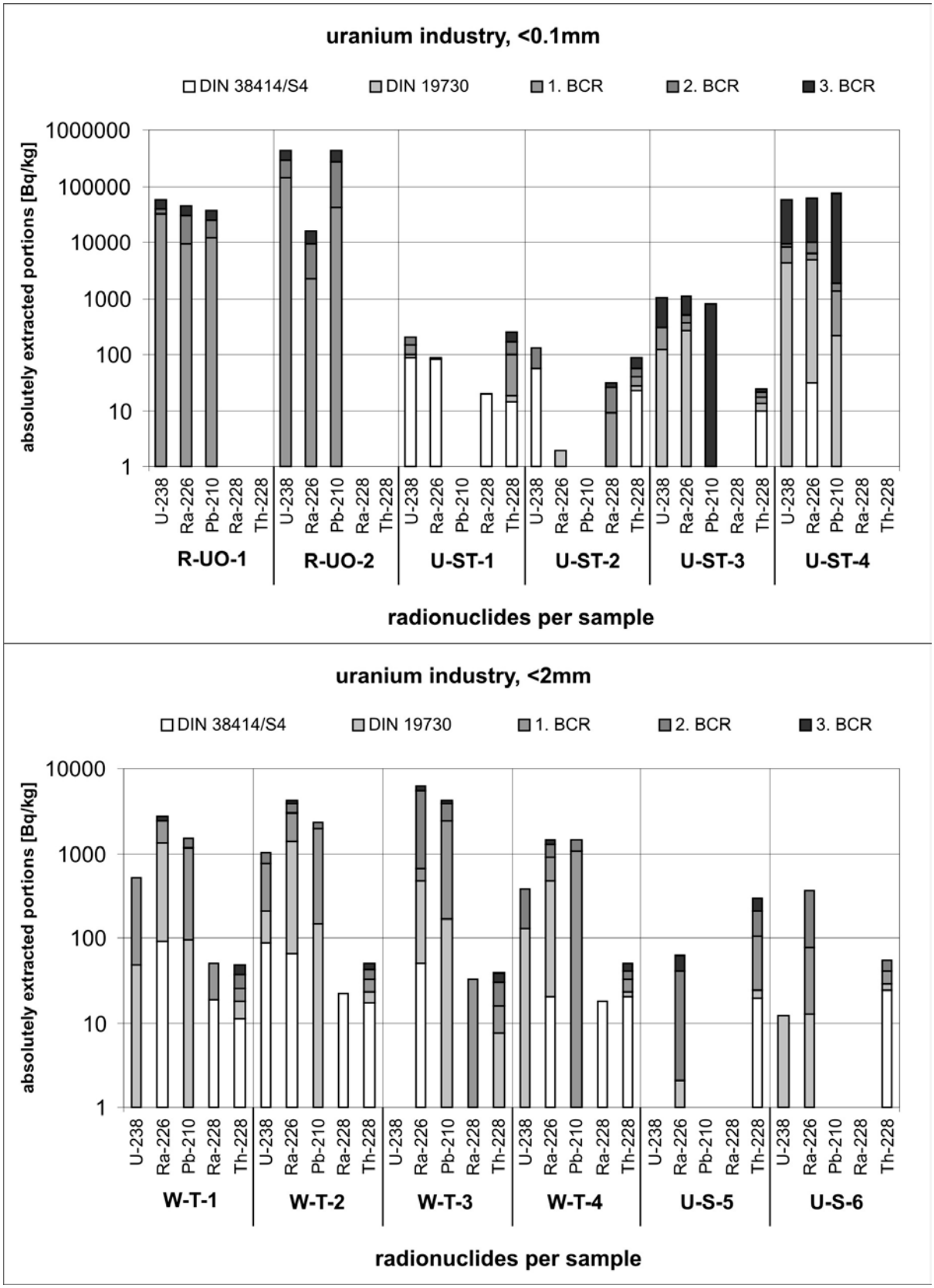

Fig. 6-21: Absolutely extracted radionuclide portions of all the uranium industry's samples; the total amount of extracted portions can exceed the initial radionuclide concentrations due to overlapping of the extractions by the three different extraction procedures.

Due to low activity concentrations in the solid tailing samples, the extracted uranium portions are also relatively low with an accentuation of the plant available and grain surface adsorbed fractions. The uranium's easy availability from the remnants of the production process

can be explained by the cracking of uranium bearing minerals in frame of the extraction. After that, the attacked uranium which is not removed got fixed by weak bindings in the tailing waste. According to fig. 6-21, this is also valid for the progenies ^{226}Ra and ^{210}Pb, they are mostly present in easily exchangeable fractions, in case of ^{226}Ra including the water soluble one. This supports the statement of KRIZMAN et al. (1995), who assumed a co-leaching of the uranium's progenies. Furthermore, a removal of the radionuclides from the tailings' surface within the pond as presumed in chapter "5.1.7 Uranium industry" must be considered, too. The proven easy availability of the radionuclides from tailings also explains the contamination of the sediment U-S-6, which was taken downstream of a tailing pond. Despite the fact that the sample comes from the Czech Pribram mining area, the environmental influence of not sealed tailing ponds or some having an uncontrolled rain water discharge is shown (see chapter "5.1.7 Uranium industry"). Once precipitated in that sediment, the radionuclides are hardly mobilised, ^{226}Ra is mainly bound to iron and manganese oxides. The background sample U-S-5 provides only very low amounts of ^{228}Th.

^{238}U is the radionuclide of interest in case of the raw and stockpile materials, ^{226}Ra is the relevant one for the waste and unwanted by-products, therefore both are presented separately in fig. 6-22 according to their correlation of leached versus initial activity concentrations. The samples U-ST-1 and U-ST-2 are excluded from the uranium plot due to their absolutely low initial activity concentrations. It is obvious that there is no preferred type of bounding in the milled sandstone raw materials and stockpile dead rocks as well. U-ST-3 does not provide any recognisable uranium portions, whereas U-ST-4 having been identfied to carry pure pitchblende spheroids (UO_2) on its rock surface (see appendix, chapter "A-1 Material descriptions") is determined to have fixed the uranium by far mostly in the oxidisable fraction, all the other extraction fractions step back. This is the opposite leaching behaviour as one should suggest, at least a weak preferation of the reducible state can be expected. The sandstones R-UO-1 and R-UO-2 being derived from the same rock layer in Slovenia show also no maximum for a special type of bounding. The water and plant availability is never proven and all the three BCR fractions contain same leached activity concentrations, more or less.

The background sediment U-S-5 is not affected by any ^{226}Ra and is therefore not able to provide some. The contaminated sample U-S-6 is characterised by a preferred oxidic type of bounding (2. BCR fraction), which can be explained by the presence of ferric oxides in the river sediment. This is in contrast to FEIGE & WIEGAND (1999), who observed ^{226}Ra being mainly fixed on clay minerals' surfaces in sewer sediments, which are affected by radium bearing brines from hard coal mining. This scenario is comparable with radium bearing waters coming from the Czech tailing pond, but the result differs. The Slovenian tailings are mostly determined to carry ^{226}Ra in easily available bindings such as surface adsorbed and plant available ones. One exemption is W-T-3, which contains the by far most of the radium being bound to iron and manganese oxides. This seems to be due to the acidification in frame of the uranium leaching by sulphuric acid, which results in huge amounts of many co-leached heavy metals such as strontium and manganese in the tailings (MERKEL & DUDEL, 1998). Strontium is an earth-alkaline element like radium, so an easy substitution must be taken into consideration. A clear statement about the influence on the radionuclides' leaching behaviour by growing again of new sulphuric acid caused

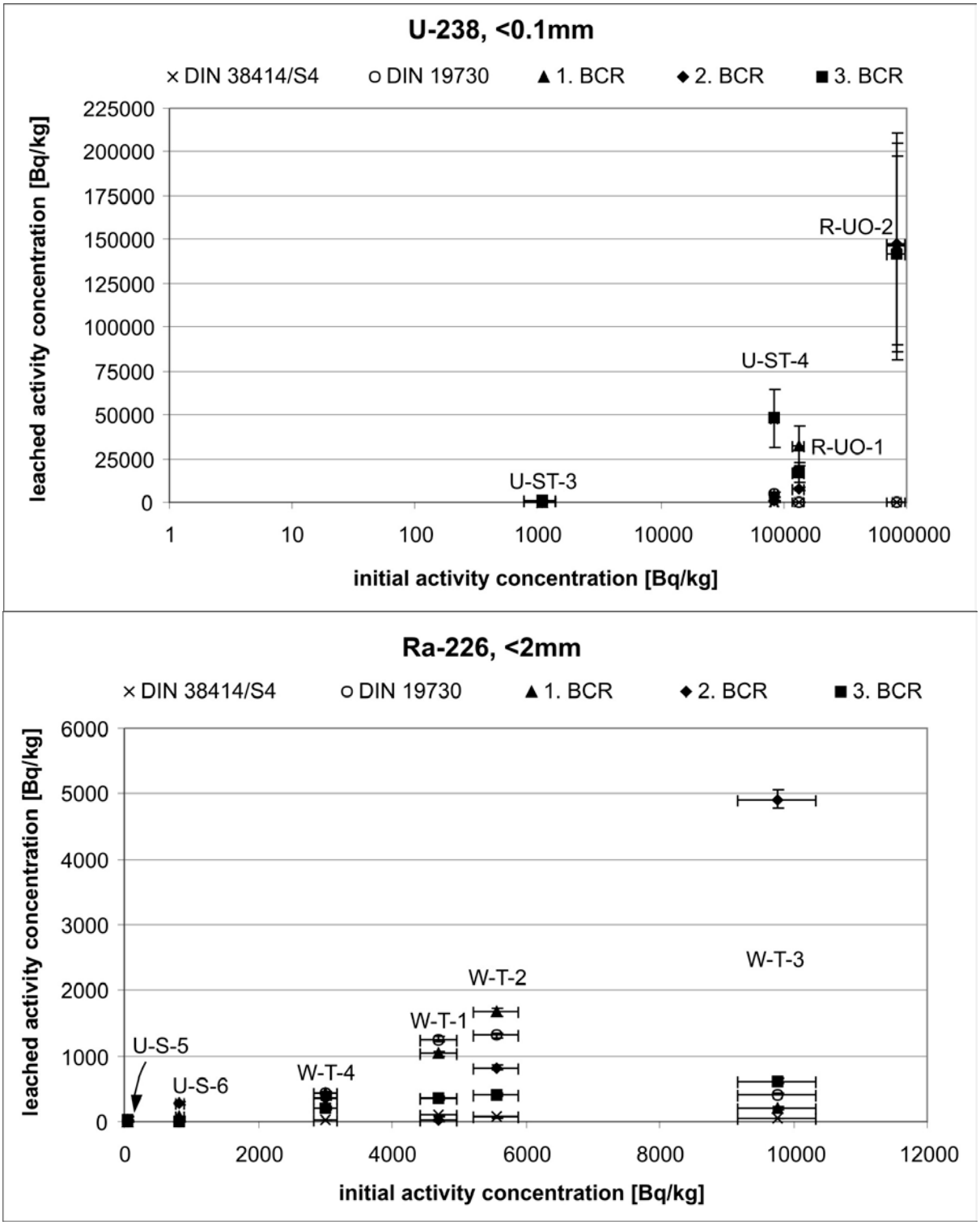

Fig. 6-22: Correlation of the ^{238}U (raw materials and stockpiles) and ^{226}Ra (wastes and unwanted by-products) specific activities in the extracted fractions versus the initial concentrations in the solid starting materials; given errors quote to 2σ-reliability.

by sulphuric compounds in the tailings as mentioned by BELEITES (1992) is not enabled, but a general easy availability of ^{238}U, ^{226}Ra and ^{210}Pb from the tailings must be emphasised.

6.2.8 Judgement of the investigation procedures

The method of measuring extraction liquids by gamma-spectrometry offers the opportunity to determine radionuclides simultaneously without any expended procedure like isolating ^{226}Ra radiochemically. The number of detected gamma-ray emitting radionuclides and their measuring reliability only depend on the calibration of the gamma-spectrometry, which can be adapted on special requests by using different standards or extending the measuring time. In frame of measuring the extraction liquids presented in this thesis, the radionuclides' different detection abilities become also clear as it is common for solid substances. In case of using progenies for determining radionuclides, the time of measurement depends on that radionuclide of the longest half-life, in this study the waiting time was set to 80 days for the establishment of equilibrium between ^{238}U and ^{234}Th.

The extraction of uranium itself seems to come along with some troubles as supposed in chapter "6.2.7 Uranium industry". The applied BCR extraction procedure does not leach the uranium in that way as to be expected due to the obvious presence of pitchblende on the rock's surface. But this is caused by the relatively weak interruption power of the used extraction liquids and all the widely applied scientific leaching procedures such as the TESSIER (1979) or ZEIEN & BRUEMMER (1989) variations are based on similar chemical solutions. In order to extract uranium it needs really strong chemicals like sulphuric acid and others as presented in chapter "3.7.1 Extraction process" being based on a lengthy and complicated industrial process, so the ability to extract uranium in frame of scientific procedures is limited by their chemical solutions for that reason alone.

Another significant characteristic is the abundant presence of ^{228}Th in many of the extraction liquids, also when no enhanced ^{232}Th and progenies' activity concentrations are to be expected. This is due to the measuring technique of using its progeny ^{208}Tl as the thorium's substitute, which can be determined very easily and reliably by its undisturbed and strongly emitted gamma-line at 583keV of almost 85% yield per decay besides 861keV, too, so extremely low detection limits are enabled.

In order to evaluate the influence of different grain sizes on the radionuclides leaching behaviour, some samples having been delivered in sufficient volumes were divided into both grain sizes <2mm and 0.1mm. The first fraction is obtained by sieving, the latter by milling. The materials of the aluminium and the uranium industry are taken for this investigation, their absolutely extracted fractions per radionuclide and sample are summarised in fig. 6-23. All the aluminium samples do not show any significant difference, they are rather comparable for both grain sizes apart from ^{210}Pb being leached from the <2mm fraction of R-AO-1, but not from the milled one. This is surprising since the milled grain's specific surface is considerably enhanced compared with those of the only sieved fraction and therefore higher leached radionuclide concentrations could be expected. But this phenomenon is also proven by the uranium industry's materials, in the very most cases the extraction liquids of both grain sizes do contain similar activity concentrations. Exemptions are the totally leached amounts of uranium from the sample W-T-1, which are higher from the milled fraction, and in case of W-T-3 the really low amount of ^{228}Ra was proven to be water soluble from the milled portion instead of being bound to iron and

manganese oxides as determined for the sieved one. The especially poorly contaminated sediment U-S-5 shows the most deviations, the milled material does provide more radionuclides and in higher dimensions, which is valid for the sediment U-S-6 in some extent, too. By having a closer look on ^{226}Ra, which is quite a representative for the waste and unwanted by-products, the general poor influence of the grain size is shown once again (fig. 6-24): almost all the extraction liquids' activity concentrations are similarly developed for both fractions, <2mm and <0.1mm, just slightly higher activity concentrations are determined for all the milled samples.

In summary, the influence of the grain size is much lower as one could expect and there is no specific radionuclide being especially affected. Therefore, the materials' sieved fraction <2mm

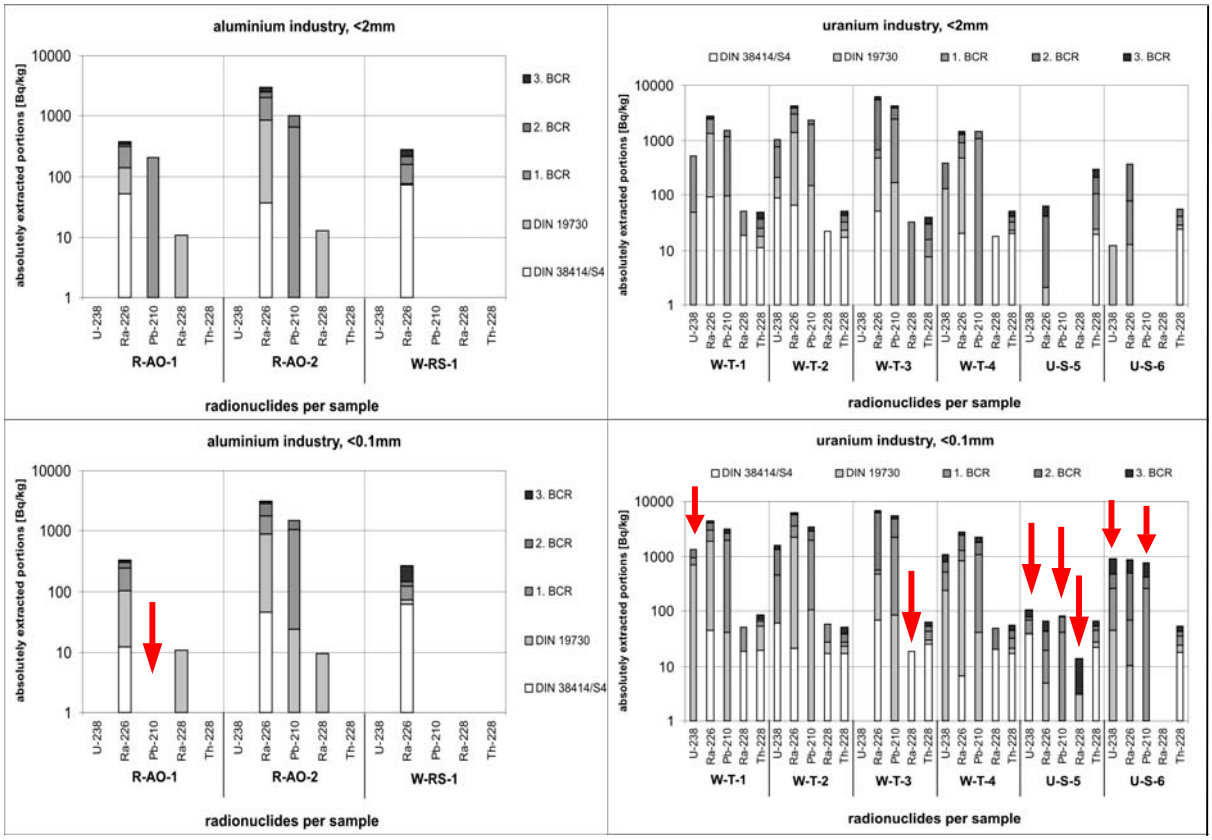

Fig. 6-23: Absolutely extracted fractions from all the materials of the aluminium and the uranium industry's waste materials and unwanted by-products according to both grain sizes <2mm and <0.1mm; arrows mark differences.

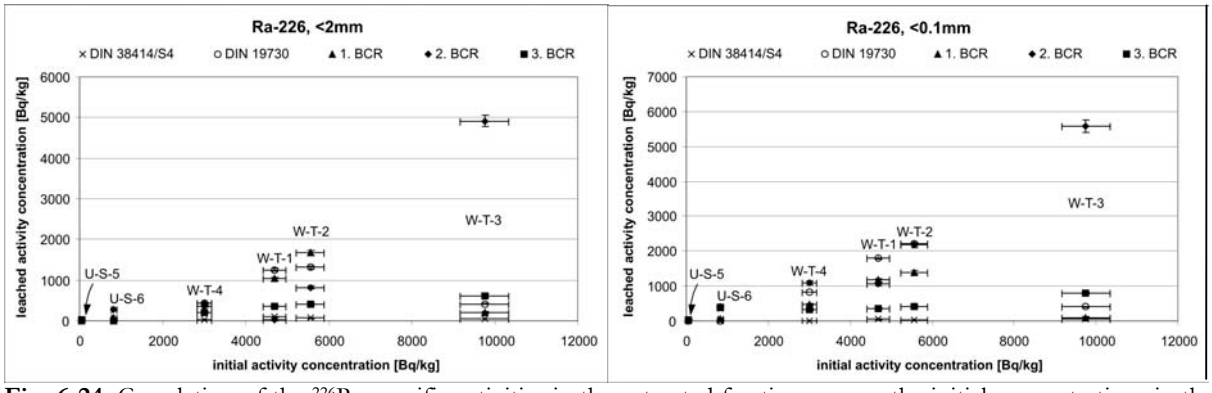

Fig. 6-24: Correlation of the ^{226}Ra specific activities in the extracted fractions versus the initial concentrations in the uranium industry's waste materials and unwanted by-products according to both grain sizes <2mm and <0.1mm; given errors quote to 2σ-reliability.

can be reliably used for the investigation of many samples since milling the substances is time consuming, the deviations from the milled ones do not interfer the results significantly. The possible phenomenon of fewer leached amounts of radionuclides from milled materials was also observed by LEOPOLD et al. (2007), who investigated tailings from Polish hard coal mining being separated into <2mm and <0.2mm grain size for extraction according to the BCR procedure. Almost a half of the extractants from the <2mm portions do contain higher activity concentrations than the milled ones, the authors attributes this effect on the material arrangement during filling the tailing pond and some mineral separation by sieving. So, in order to reach the highest leachable amounts of radionuclides it is not absolutely demanded for the milled fraction. Therefore, the milled substances resulting from the refractory industry (W-FD-1 and P-FZM-2), which were just available in milled versions, can be taken for being representative (fig. 6-12, 6-13).

6.3 Radon emanation rates

Both decay series, the uranium and the thorium as well, contain one isotope of the chemically inert volatile element radon, which is therefore called a noble gas. It results from the decay of radium, that one part of the uranium's series (^{222}Rn) from ^{226}Ra with a half-life if 3.6d and the other (^{220}Rn, also called thoron) from ^{224}Ra of the thorium series, half-life of 55s. Due to that much shorter half-life, ^{220}Rn does not pose as a serious problem from a transport and exposure point of view and is excluded within this thesis. The radiological risks associated with the handling and disposal of materials are therefore primarily due to the contamination with ^{226}Ra and its progeny ^{222}Rn, its inhalation has been associated with an increased risk of lung cancer (NAS, 1988). These risks are dependent on the overall rate at which ^{222}Rn is transported to the surrounding atmosphere via advection or diffusion and subsequently released from the material matrix. The term "radon emanation" is defined as the fraction of radon atoms formed in a solid that escapes from the solid and is free to migrate. The physical properties of the ^{226}Ra bearing material largely determine the radon emanation from the material. According to WHITE (2001), these physical properties include:

1. the distribution of ^{226}Ra within the material
2. whether the material is massive or granular
3. the type and magnitude of the material's porosity
4. the moisture content in the material
5. the effective ^{222}Rn diffusion coefficient of the material

The maximum emanation rates are reached by water saturation of the solid material, because the liquid slows down the recoil energy of the formed radon atom, so a penetration of the next surrounding grains is interfered, and acts also as a blocking layer for the grains' surfaces resulting in a reduced adsorption (PELLEGRINI et al., 1996). Additional information on emanation mechanisms is given by TANNER (1980), RAMA & MOORE (1984) and WIEGAND (1999).

In this thesis, the emanation is investigated without any water, because realistic coefficients for the handled materials, not maximum dimensions are in the focus. Despite the fact that the emanation increases with smaller grain sizes and therefore enhanced surfaces, only the fractions <2mm are taken in frame of the investigations for the same reason. The industry types "Hard coal extraction" and "Thorium compounds industry" are not investigated for their radon emanation potential due to small sample volumes respectively thoron must be assumed for the main volatile component.

6.3.1 Phosphate industry

In fig. 6-25, the emanation rates of all the phosphate industry's materials are plotted versus the respective ^{226}Ra content, the emanation coefficients are also presented. As obvious, the phosphate ores and the phosphogypsum waste as well are characterised by really low emanation coefficients, but in case of R-PO-1 it means nevertheless moderate absolute emanation rates due to the high initial ^{226}Ra activity concentration. Phosphogypsum is usually heaped up in stockpiles close to the production plants (AGUADO et al., 2004), but due to the low emanation coefficient of 1.4%, in this case the radiological hazard potential is neglectible. This result is contrary to that value given by JANSSENS (1984), who reported an emanating coefficient of 14% for Belgian phosphogypsum, but detailed information about grain size or moisture content are not reported. Another characteristic is the relatively high dimension of the fertiliser's emanation coefficients. This might be caused by the fact that the raw materials and the waste consist of dense grain compounds, whereas the fertiliser spheroids are produced completely new, so the grain structure

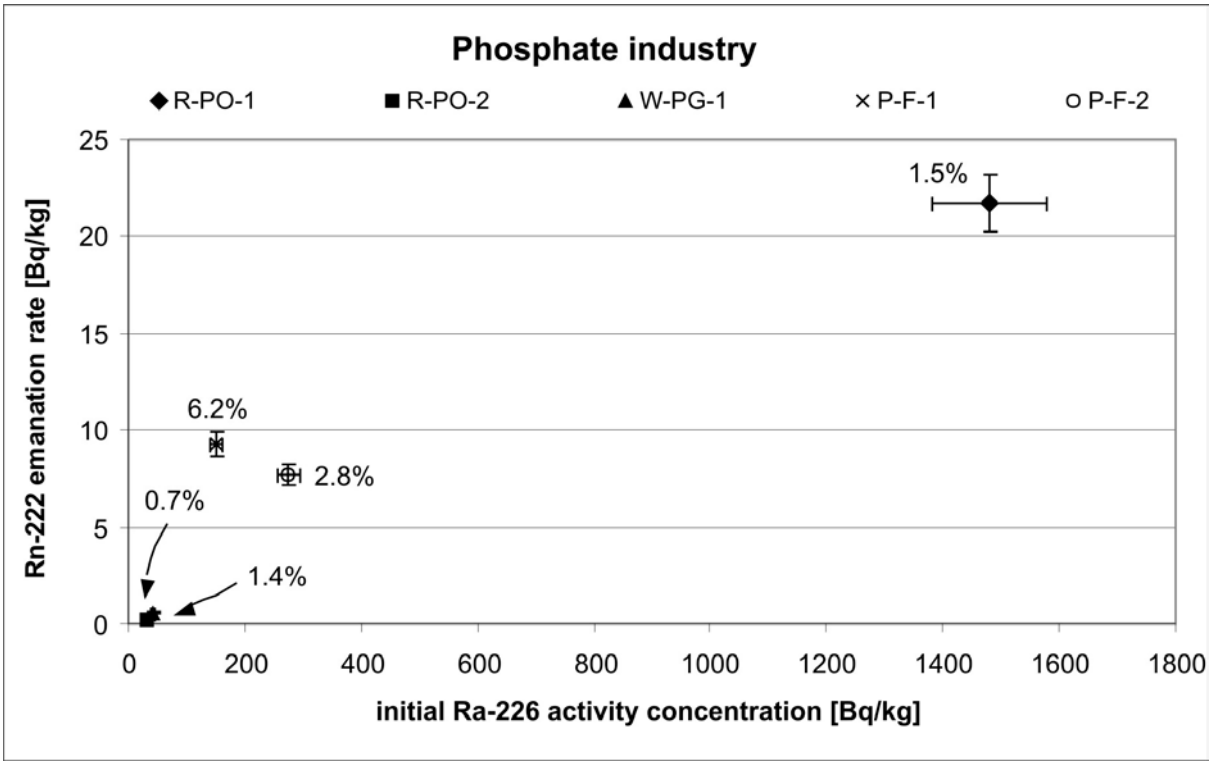

Fig. 6-25: Correlation of the initial ^{226}Ra specific activities versus the ^{222}Rn emanation rates in the phosphate industry's materials, emanation coefficients given in [%]; given errors quote to 2σ-reliability.

is not established in that density as the rocks and granulars are. The result is an easier escaping pathway for the radon atoms. A positive correlation with the ^{226}Ra's type of bounding is not recognisable, all the materials are determined to contain really low radium concentrations in the easily available fractions (DIN 38414/S4, DIN 19730, 1. BCR) (fig. 6-6).

6.3.2 Aluminium industry

In case of the materials of the aluminium production, all samples were delivered in sufficient volumes to separate them into both grain size fractions, <2mm and <0.1mm (fig. 6-26). The Boke bauxite rock (R-AO-1) shows an emanation coefficients of 5.3% for both grain sizes, whereas the Trombeta's bauxite (R-AO-2) is proven to emanate radon generally in higher dimensions, but with its maximum from the <2mm fraction than from the milled material. This is surprising since the usual ratio is the opposite, but in these cases the influence of the grain size is not recognisable (R-AO-1) or the opposite as to be expected. In general, the bauxites show some remarkable emanation coefficients, which can be attributed to the well developed porosity of the aluminium ores bein supported by a mentionable amount of weakly bound ^{226}Ra (fig. 6-9). The red sludge waste is characterised by very poor emanation rates the coefficient ranging around 1.6% also without any difference between the grain sizes. RADULESCU & POPESCU (2002a) reported ^{222}Rn concentrations of 248Bq/m^3 for the air above the tailing's surface, which is a moderately enhanced value, but due to relatively low ^{226}Ra activity concentrations in the material it can not be caused by the determined very low emanation coefficient. One explanation could be that the red sludge waste in the pond does contain a certain amount of moisture due to transportation as suspension in the pipeline from the processing plant to the basin (see chapter "3.2.3 Investigation site") beside some rain fall, too. The investigated sample was delivered in dried state for transportation aspects, so a lower emanation power is the result.

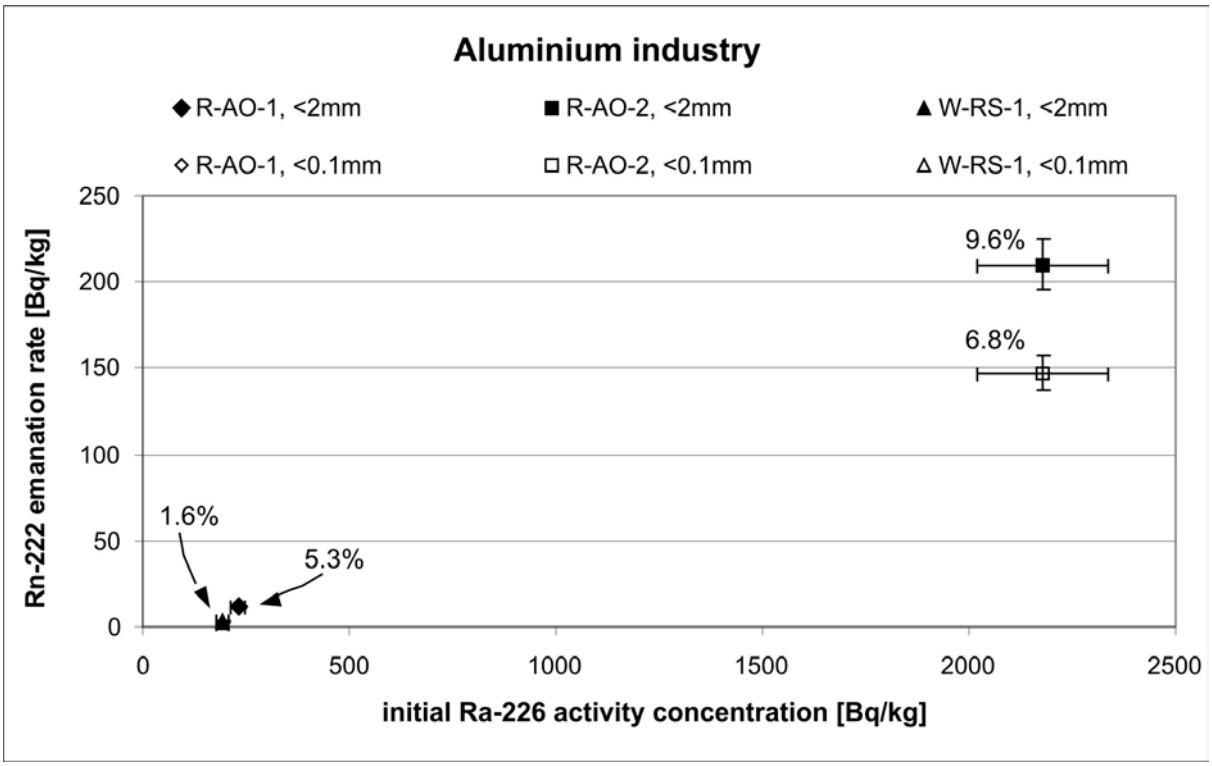

Fig. 6-26: Correlation of the initial ^{226}Ra specific activities versus the ^{222}Rn emanation rates in the aluminium industry's materials, emanation coefficients given in [%]; given errors quote to 2σ-reliability.

6.3.3 Refractory industry

Those materials having been delivered as granulars (R-ZS-1 and P-FZM-1) are investigated for both fractions, the sieved and the milled one, the others were just available in milled versions. In general, all the substances occurring in frame of the refractory production show extremely low emanation rates and coefficients (fig. 6-27). R-ZS-1 emanates more radon from the milled portion than from the sieved one, which is in line with expectations and also valid for the product P-FZM-1. The zircon sand's low emanation dimensions can be attributed to the very dense mineral structure of the zircon crystals, so a radon escape is almost completely prohibited. This seems to be also transferable on the produced filter dust waste and the products as well in some extent, which means the doubtless high ^{226}Ra concentrations in the mullite products must be strongly bound to compounds. As shown in fig. 5-39 until 5-46, there is no mentionable ^{226}Ra available from those materials, almost all is left in the residuals. The filter dust does provide some easily available radium indeed, but in relation to relatively low initial activity concentrations (295Bq/kg).

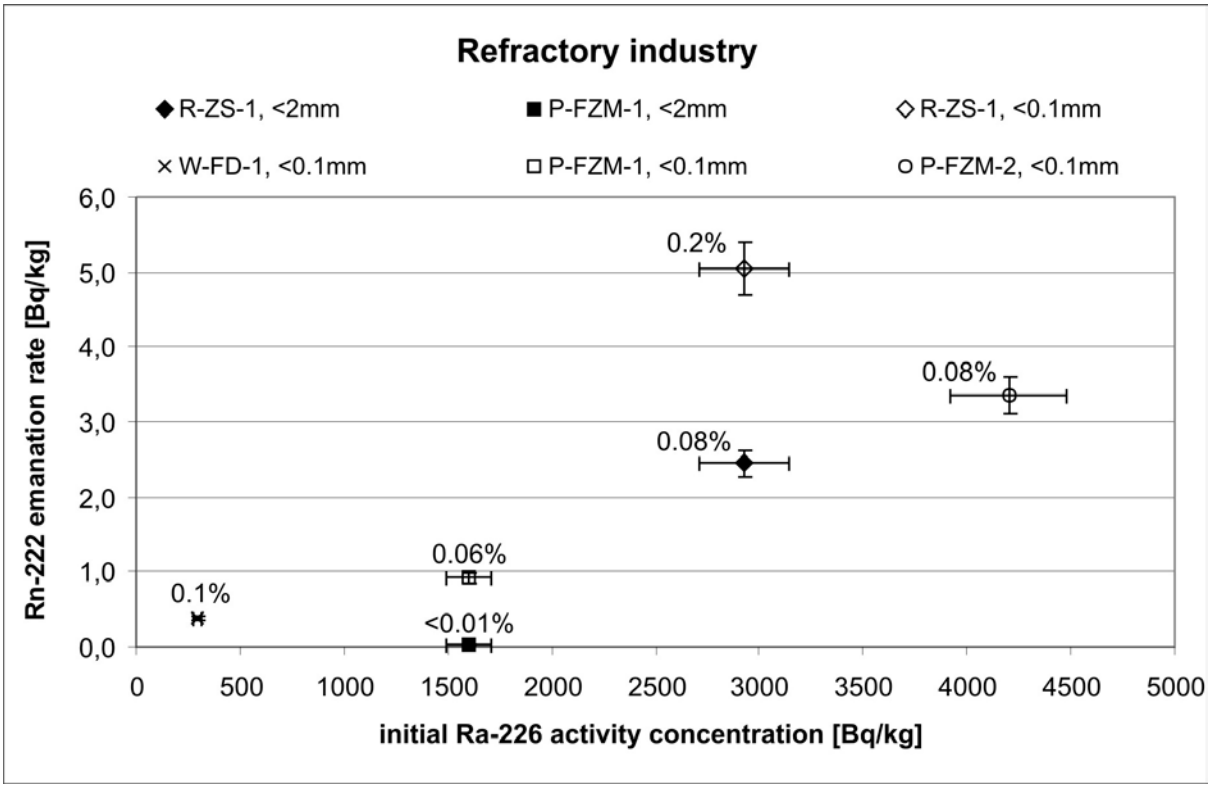

Fig. 6-27: Correlation of the initial ^{226}Ra specific activities versus the ^{222}Rn emanation rates in the refractory industry's materials, emanation coefficients given in [%]; given errors quote to 2σ-reliability.

6.3.4 Crude oil exploitation

The radon emanation behaviour of the sludge and scale samples is summarised in fig. 6-28. As shown, the sludge emanates much more radon than the scale and there is also a rough positive correlation for the sludge: the higher the initial ^{226}Ra activity concentration the higher the emanation rates. But nevertheless, the respective coefficients are rather low, which is also valid

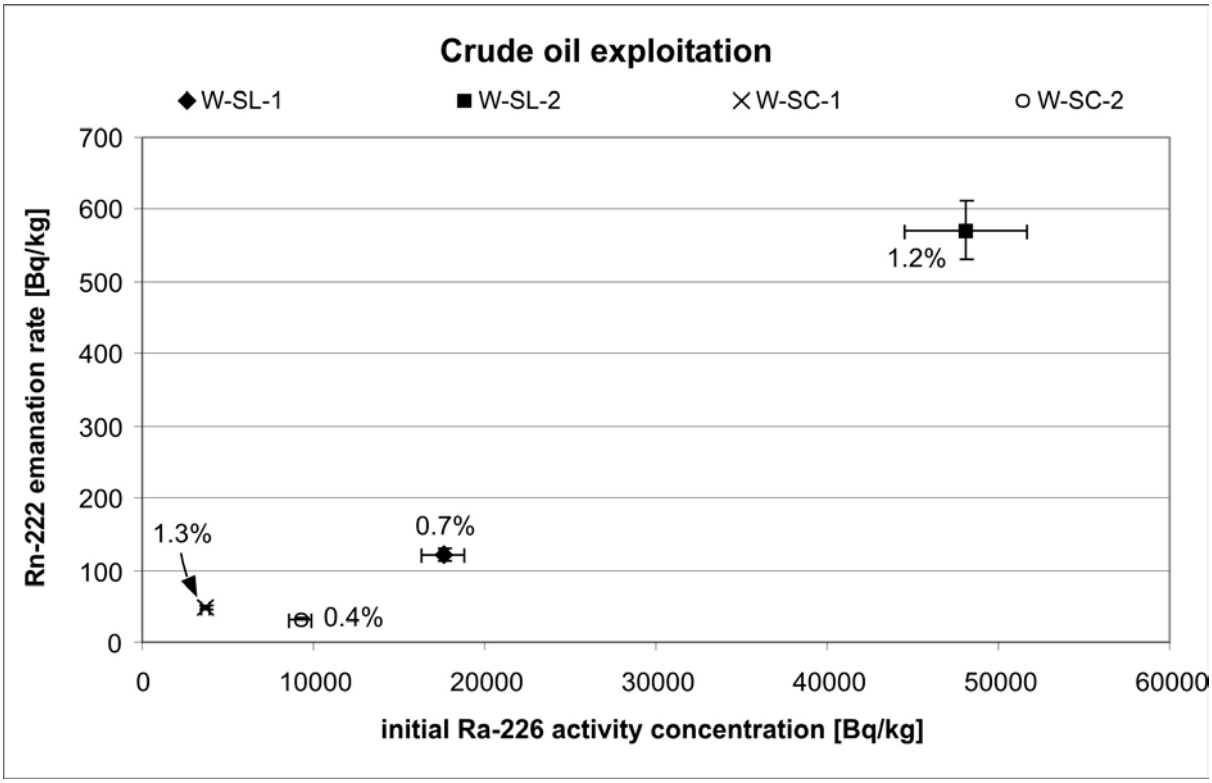

Fig. 6-28: Correlation of the initial ^{226}Ra specific activities versus the ^{222}Rn emanation rates in the crude oil exploitation's materials, emanation coefficients given in [%]; given errors quote to 2σ-reliability.

for the scales. The latter are proven to emanate only relatively low amounts of radon. This deviations are caused by the different type of material. Both sludge samples were delivered in an oily state, which also has not changed after drying. Therefore, a certain amount of liquid is always present in the sample material leading to higher emanation rates. In contrast, scale usually comprises barite for a significant portion (GODOY & PETINATTI DA CRUZ, 2003), so a stable crystal lattice reduces the radon escape evidently; sludge does not contain such a dense precipitate (GODOY et al., 2005).

6.3.5 Uranium industry

The emanation rates and coefficients of all the materials occurring in frame of the uranium industry are summarised in fig. 6-29. The four tailing samples show very similar emanation characteristics, the rates range around 100Bq/kg, which corresponds to respective coefficients of roundabout 2%. The raw material R-UO-1 exceeds those rates by a magnitude of more than 10, the coefficient is in same range. These results are in good agreement with the ^{226}Ra's determined types of bounding especially for the tailings, a huge portion is proven to be easily exchangeable in all cases (fig. 6-21). The high emanation rates get put into perspective by KRIZMAN & STEGNAR (1992), who investigated the radon hazard potential in the vicinity of the former "Zirovski Vrh" uranium mine. They found slightly enhanced radon concentrations in air of 50Bq/m^3 close to the mine (~ 0.3km), which then decreases to 14Bq/m^3 in a distance of roughly 20km. The radon's exact origin is not defined, as possible contributions the installations such as ventilation shafts, the uranium mill, the tailing pond and the ore deposits themselves are taken into consideration as

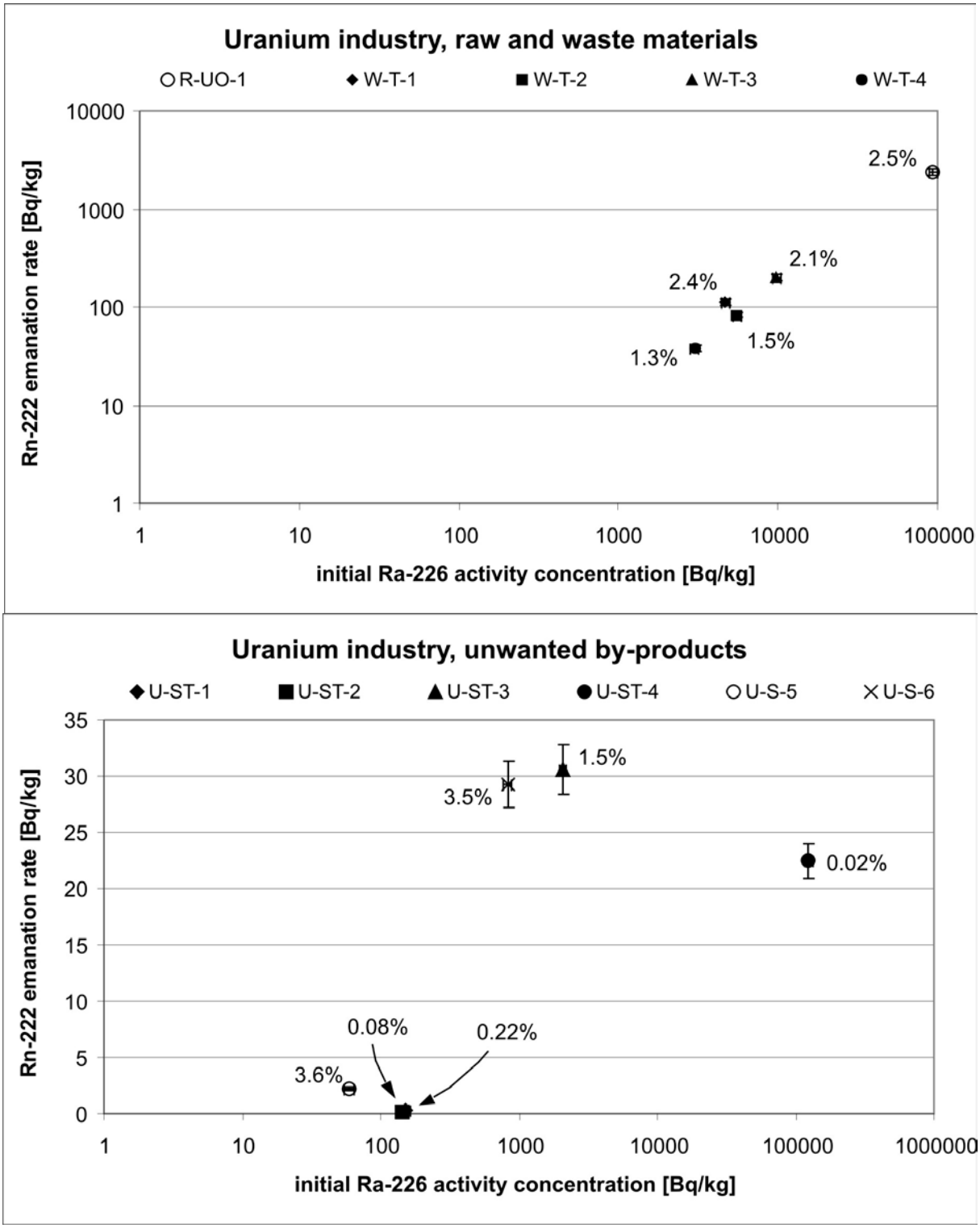

Fig. 6-29: Correlation of the initial ^{226}Ra specific activities versus the ^{222}Rn emanation rates in the uranium industry's materials, emanation coefficients given in [%]; given errors quote to 2σ-reliability.

a melange. The obtained emanation rates mentioned above support a decisive portion of the tailings and elevated radon air concentrations must be assumed on the tailings' surface, ROJC & JOVANOVIC (2005) calculated an annual radon emission of 2 TBq/a just from the investigated tailing pond. According to KRIZMAN & STEGNAR (1992), there is a special topographical situation attention must be paid for, because the former uranium production plant and the surrounding installations are located in a long and narrow valley (fig. 3-13b), where steady, but slowly winds in

a prevailing South-North direction and temperature inversions occur for more than half a year. These meteorological conditions do not allow radon to dispers immediately, which then leads to some enhanced concentrations in air. Therefore, the tailings' covering with a clayey gravel of 0.6m thickness is still in progress, first results prove a radon release reduction by 90% down to 0.2TBq/a (ROJC & JOVANOVIC, 2005).

In comparison with those Slovenian raw and waste materials the Czech unwanted by-products have only a rather low radon impact (fig. 6-29). The slags' (U-ST-1 and U-ST-2) emanation rates are close to zero, the dead rocks U-ST-3 and U-ST-4 emanate some few amounts. Since all samples are almost unporous (appendix, chapter "A-1 Material descriptions"), the reason for this difference is simply that the slags do contain just very low ^{226}Ra activity concentrations whereas the dead rocks are proven for some hundreds respectively thousands of Bq/kg, from which a certain low amount is free to emanate due to some easily available ^{226}Ra (fig. 6-21). Both the sediments are characterised by same emanation coefficients of 3.5% underlining their same origin, the radium contaminated one shows a higher emanation rate caused by some poor amounts of weakly bound radium (fig. 6-21). Since the river they were taken from is a narrow one with only small riverbanks and no flood plains along, a common water covering can be assumed for the sediments resulting in reduced emanation rates. According to FEIGE & WIEGAND (1999), the higher radon exhalation rates occur on overbank deposits and not on the riverbanks.

6.3.6 Judgement of the radon emanation results

In summary, it is to be pointed out that the measured radon emanation behaviour is not always in line with expectations, which means sometimes theres is no obvious interaction between the emanation rates and the determined types of bounding of ^{226}Ra. This is visible in particular from the phosphate industry's samples. An explanation is that the radon release is controlled by many factors as mentioned in chapter "6.3 Radon emanation rates", so a combination of some must be assumed (SCHUMANN & GUNDERSEN, 1996). For reliable statements a charge of samples should be investigated, but that was not enabled in frame of this thesis due to limited access to the concerned materials. Therefore, the given data should be considered as a clue.

7 Leachate prospects

In order to determine the radionuclide's easily releasable volumes from TENORM, which can lead to substantial environmental pollution, especially both the German extraction procedures DIN 38414/S4 for the pathway "solid-water" and DIN 19730 for the pathway "solid-plant" are useful, whereas the European BCR-procedure gives mainly information about the radionuclide's stronger chemical types of bounding. In Germany, those DIN procedures are proposed by the Federal Soil Protection Ordinance (Bundes-Bodenschutz-Verordnung BBodSchV) for the evaluation of anorganic pollutants' release potentials from soils, if no direct water samples can be taken (BBODSCHV, 1999). This scenario is transferable to the TENORM samples presented in this study. With regard to radionuclide contaminations, such leaching procedures are not officially proposed neither by European nor by German authorities up to now. But GELLERMANN & SCHULZ (2006) investigated DIN 38414/S4 extracts from sediments influenced by hard coal mining (equal to those presented in chapter "3.5 Hard coal extraction") and thorium contaminated soils taken at Oranienburg (equal to those presented in chapter "3.6 Thorium compounds industry") by gamma-spectrometer for their radionuclide inventory.

POSCHNER & SCHALLER (1995) developed migration models on the basis of partition coefficients for radionuclide emissions from stockpiles, which then were further used for definitions of supervising thresholds as mentioned in annex XII of the German Radiation Protection Ordinance (STRSCHV, 2001). The distribution of radionuclides in frame of migration models is given by the partition coefficient k_d, which is defined as follows:

$$k_d = \frac{a^s}{c^w} \qquad \text{[equ. 20]}$$

a^s: specific activity fixed at solid [Bq/kg]
c^w: leached activity concentration in the water [mBq/l = Bq/m³]

Those migration models are assumed to be kept in equilibrium between fixed and leached phase, so the total of both will migrate simultaneously. The adsorption retards the migration rate in dependence of the rock's density and porosity, which is taken into account by a so called "retardation factor". Since this model is based on the activity adsorbed at the solid, it is just slightly useful, because that amount of activity migrates quickly and represents only a short-term radionuclide source. Instead, GELLERMANN & SCHULZ (2006) preferred the term "transfer factor" for substance release processes resulting from soil contamination. The transfer factor TF is defined as follows:

$$TF = \frac{c^w}{a^s} = \frac{1}{k_d} \qquad \text{[equ. 21]}$$

TF: transfer factor [g/m³]
c^w: radionuclide's activity concentration in the leachate [mBq/l = Bq/m³]
a^s: specific activity of the rock respectively solid material [Bq/g]

The transfer factor TF characterises the radionuclide transfer from the solid material into the leachate as a phenomenologic code number and is reciprocal to the partition coefficient k_d. There is quite a difference to the k_d-value, because TF is a parameter for the radionuclide's release potential and is related to experimentally obtained liquids such as extracts and to specific activities of solid materials. In contrast, k_d-values are focused on the transport in a state of adsorption equilibrium. Therefore, the method of calculating transfer factors is used for the purpose of leachate prospects as presented in the following. Nevertheless, a lot of k_d-values are published for the initial radionuclides uranium and thorium, but without any regard to their progenies.

Since the hard coal samples were not investigated for their water and plant availability due to low sample amounts, those are excluded in the following calculations.

7.1 Pathway "solid-water"

The pathway "solid-water" is given by the German extraction procedure according to DIN 38414/S4. In order to calculate the radionuclides' transfer factors from the TENORM solids into water, the activity concentrations in the extract are related to the respective initial activity concentrations according to equation 21. Those calculations are based on the values presented in the appendix "A-4 Radionuclide portions extracted by DIN 19730 and DIN 38414/S4 procedures", the resulting transfer factors are summarised in table 7-1.

Table 7-1: Calculated transfer factors TF given in [g/m³] for the pathway "solid-water" for all TENORM samples.

Phosphate industry					
	R-PO-1, <2mm	**R-PO-2, <2mm**	**W-PG-1, <2mm**	**P-F-1, <2mm**	**P-F-2, <2mm**
^{238}U	n.d.	n.d.	n.d.	n.d.	28,400
^{226}Ra	n.d.	n.d.	n.d.	n.d.	2900
^{210}Pb	n.d.	n.d.	n.d.	n.d.	n.d.
^{228}Ra	n.d.	n.d.	n.d.	n.d.	n.d.
^{228}Th	160,000	24,400	54,000	214,000	n.d.

Aluminium industry			
	R-AO-1, <2mm	**R-AO-2, <2mm**	**W-RS-1, <2mm**
^{238}U	n.d.	n.d.	n.d.
^{226}Ra	21,600	1800	41,000
^{210}Pb	n.d.	n.d.	n.d.
^{228}Ra	n.d.	n.d.	n.d.
^{228}Th	n.d.	n.d.	n.d.
	R-AO-1, <0.1mm	**R-AO-2, <0.1mm**	**W-RS-1, <0.1mm**
^{238}U	n.d.	n.d.	n.d.
^{226}Ra	4300	2200	31,000
^{210}Pb	n.d.	n.d.	n.d.
^{228}Ra	n.d.	n.d.	n.d.
^{228}Th	n.d.	n.d.	n.d.

n.d.: not detected

continuation Table 7-1: Calculated transfer factors TF given in [g/m³] for the pathway "solid-water" for all TENORM samples.

Refractory industry				
	R-ZS-1, <2mm	**W-FD-1, <0.1mm**	**P-FZM-1, <2mm**	**P-FZM-2, <0.1mm**
^{238}U	n.d.	n.d.	n.d.	n.d.
^{226}Ra	n.d.	n.d.	n.d.	n.d.
^{210}Pb	n.d.	40	n.d.	n.d.
^{228}Ra	n.d.	n.d.	n.d.	n.d.
^{228}Th	3000	22,500	6500	2700
Crude oil exploitation				
	W-SL-1, <2mm	**W-SL-2, <2mm**	**W-SC-1, <2mm**	**W-SC-2, <2mm**
^{238}U	n.d.	n.d.	n.d.	n.d.
^{226}Ra	120	45	n.d.	n.d.
^{210}Pb	n.d.	n.d.	n.d.	300
^{228}Ra	n.d.	100	n.d.	n.d.
^{228}Th	500	160	1130	1170
Thorium compounds industry				
	U-SO-1, <2mm	**U-SO-2, <2mm**	**U-SO-3, <2mm**	**U-SO-4, <2mm**
^{238}U	n.d.	n.d.	n.d.	n.d.
^{226}Ra	n.d.	n.d.	n.d.	44,400
^{210}Pb	n.d.	n.d.	n.d.	n.d.
^{228}Ra	22	n.d.	270	n.d.
^{228}Th	7	n.d.	280	64,800
Uranium industry				
	W-T-1, <2mm	**W-T-2, <2mm**	**W-T-3, <2mm**	**W-T-4, <2mm**
^{238}U	n.d.	5000	n.d.	n.d.
^{226}Ra	2070	1200	550	730
^{210}Pb	n.d.	n.d.	n.d.	n.d.
^{228}Ra	64,500	79,300	n.d.	67,900
^{228}Th	37,500	66,600	n.d.	70,000
	W-T-1, <0.1mm	**W-T-2, <0.1mm**	**W-T-3, <0.1mm**	**W-T-4, <0.1mm**
^{238}U	n.d.	3500	n.d.	n.d.
^{226}Ra	1020	410	750	330
^{210}Pb	n.d.	n.d.	n.d.	n.d.
^{228}Ra	64,500	62,000	60,600	78,500
^{228}Th	65,600	66,600	87,000	60,000
	U-ST-1, <0.1mm	**U-ST-2, <0.1mm**	**U-ST-3, <0.1mm**	**U-ST-4, <0.1mm**
^{238}U	50,800	42,500	n.d.	n.d.
^{226}Ra	58,000	n.d.	n.d.	27
^{210}Pb	n.d.	n.d.	n.d.	n.d.
^{228}Ra	65,600	n.d.	n.d.	n.d.
^{228}Th	48,400	66,600	240,000	n.d.
	U-S-5, <2mm	**U-S-6, <2mm**	**U-S-5, <0.1mm**	**U-S-6, <0.1mm**
^{238}U	n.d.	n.d.	65,600	n.d.
^{226}Ra	n.d.	n.d.	n.d.	n.d.
^{210}Pb	n.d.	n.d.	n.d.	n.d.
^{228}Ra	n.d.	n.d.	n.d.	n.d.
^{228}Th	161,500	104,000	185,000	80,700

n.d.: not detected

The most of the phosphate industry's samples show exclusively high transfer factors for ^{228}Th in dimensions of 20,000 up to 200,000g/m^3, which is a wide range; P-F-2 provides only ^{238}U and ^{226}Ra. Up to now, there are no comparison data available in literature concerning radionuclide migration of materials from the fertiliser production.

All the TENORM occurring in frame of the aluminium production are determined to contain water soluble ^{226}Ra, from which the bauxite raw materials have the lower TF's of just a few thousand g/m^3, those of the red sludge waste are between 30,000 and 40,000g/m^3; any grain size influence is not obvious. Directly comparable literature data of radium migration models for such muddy materials like the red sludge and the bauxites as well are not published, but SEELEY & KELMERS (1984) reported for an unspecified red-brown clay an uranium k_d-value of 250ml/g being equal to a reciprocal TF of 4000g/m^3. This is one magnitude lower for the radium's parent radionuclide uranium. Nevertheless, a direct comparison is not allowed due to different intentions in the calculation.

Apart from the filter dust, all the substances of the fused zirconia mullite production (refractory industry) are determined to release 3000-6500g/m^3 of ^{228}Th, which is a moderate range. The filter dust has a higher ^{228}Th transfer factor of 22,500g/m^3 and provides a very small amount of ^{210}Pb. Also for refractory materials no literature data are available.

The sludge and scale samples resulting from the crude oil exploitation show generally low transfer factors. The sludge provide some few amounts of radium and ^{228}Th for water (max. 500g/m^3). BELL & BATES (1988) published some uranium k_d-values for borehole groundwater of the same range (max. 2200ml/g being reciprocal to a TF of 450g/m^3) and also their thorium k_d-values are in good agreement (5800ml/g being reciprocal to a TF of 170g/m^3), but a direct comparison is prohibited as mentioned above. The scales' ^{228}Th transfer factors are slightly higher than 1000g/m^3, W-SC-2 releases also 300g/m^3 of ^{210}Pb, but other radionuclides are not proven to be water soluble. For this type of material no leachate data are given in literature.

The thorium contaminated soils show a differentiated water leaching behaviour. That catalyst influenced sample U-SO-1 is characterised by really low transfer factors, 22g/m^3 for ^{228}Ra and 7g/m^3 for ^{228}Th, but there is a good agreement with those data given by GELLERMANN & SCHULZ (2006), who investigated exactly the same site. They found a TF for ^{228}Ra of 20g/m^3 and for unspecified thorium of 0.1-1g/m^3 and they calculated the TF in the same way as presented in this study. Also U-SO-3 has comparable TF's especially for radium (245g/m^3 according to HGN (2001) and 270g/m^3 in this study), that of thorium is two magnitudes higher. In contrast, sample U-SO-4 exceeds those literature data in some magnitudes (more than 1000 times for radium and 10,000 for thorium).

All the Slovenian tailing samples show water soluble amounts of both radium isotopes and ^{228}Th as well. Whereas the ^{226}Ra transfer factors reach only a maximum of 2000g/m^3, the ^{232}Th progenies are calculated for some ten thousands of g/m^3. As mentioned for the aluminium industry, any grain size influence is not obvious. MERKEL & DUDEL (1998) investigated also a tailing in Germany, but they did not apply a leaching test despite the fact that they focused their attention mainly on uranium. Nevertheless, they took some water samples within the tailing and

found a maximum uranium concentration of 1500g/m^3, which is in good agreement with the values calculated for W-T-2 (the other samples are not proven to provide uranium for water). The dead rocks and sediments from the former Czech mining area are mainly characterised by ^{232}Th progenies' water solubility, but the dimensions are really high and range from 50,000 up to 240,000g/m^3. The samples U-ST-1, U-ST-2 and U-S-5 show additionally some ten thousands of g/m^3 of water leachable uranium, which is also a high dimension. In case of the sediments once again no grain size influence can be observed.

7.2 Pathway "solid-plant"

The pathway "solid-plant" is given by the German extraction procedure according to DIN 19730. In order to calculate the radionuclides' transfer factors from the TENORM solids into plants, the activity concentrations in the extract are related to the respective initial activity concentrations according to equation 21. Those calculations are based on the values presented in the appendix "A-4 Radionuclide portions extracted by DIN 19730 and DIN 38414/S4 procedures", the resulting transfer factors are summarised in table 7-2.

Table 7-2: Calculated transfer factors TF given in [g/m^3] for the pathway "solid-plant" for all TENORM samples.

Phosphate industry					
	R-PO-1, <2mm	**R-PO-2, <2mm**	**W-PG-1, <2mm**	**P-F-1, <2mm**	**P-F-2, <2mm**
^{238}U	n.d.	n.d.	n.d.	n.d.	163,000
^{226}Ra	7500	25,800	n.d.	9400	4400
^{210}Pb	n.d.	420,000	630,000	67,000	157,000
^{228}Ra	n.d.	18,750	n.d.	n.d.	n.d.
^{228}Th	180,000	24,400	60,000	340,000	n.d.
Aluminium industry					
	R-AO-1, <2mm	**R-AO-2, <2mm**	**W-RS-1, <2mm**		
^{238}U	n.d.	n.d.	n.d.		
^{226}Ra	173,000	1,790,000	10,000		
^{210}Pb	n.d.	n.d.	n.d.		
^{228}Ra	29,000	36,700	n.d.		
^{228}Th	n.d.	n.d.	n.d.		
	R-AO-1, <0.1mm	**R-AO-2, <0.1mm**	**W-RS-1, <0.1mm**		
^{238}U	n.d.	n.d.	n.d.		
^{226}Ra	186,000	180,000	32,000		
^{210}Pb	n.d.	2800	n.d.		
^{228}Ra	28,400	26,600	n.d.		
^{228}Th	n.d.	n.d.	n.d.		
Refractory industry					
	R-ZS-1, <2mm	**W-FD-1, <0.1mm**	**P-FZM-1, <2mm**	**P-FZM-2, <0.1mm**	
^{238}U	n.d.	n.d.	n.d.	n.d.	
^{226}Ra	340	6100	625	975	
^{210}Pb	n.d.	1800	n.d.	n.d.	
^{228}Ra	2600	n.d.	n.d.	2600	
^{228}Th	3500	26,200	4900	3800	

n.d.: not detected

continuation Table 7-2: Calculated transfer factors TF given in [g/m³] for the pathway "solid-plant" for all TENORM samples.

Crude oil exploitation				
	W-SL-1, <2mm	**W-SL-2, <2mm**	**W-SC-1, <2mm**	**W-SC-2, <2mm**
^{238}U	n.d.	n.d.	n.d.	n.d.
^{226}Ra	910	600	325	560
^{210}Pb	275	200	n.d.	n.d.
^{228}Ra	1300	700	n.d.	n.d.
^{228}Th	430	230	n.d.	835
Thorium compounds industry				
	U-SO-1, <2mm	**U-SO-2, <2mm**	**U-SO-3, <2mm**	**U-SO-4, <2mm**
^{238}U	n.d.	5800	15,900	n.d.
^{226}Ra	3300	2100	13,600	61,100
^{210}Pb	n.d.	5000	n.d.	n.d.
^{228}Ra	5400	26,900	28,900	n.d.
^{228}Th	400	2900	2600	n.d.
Uranium industry				
	W-T-1, <2mm	**W-T-2, <2mm**	**W-T-3, <2mm**	**W-T-4, <2mm**
^{238}U	15,400	30,000	n.d.	35,000
^{226}Ra	131,000	113,000	22,300	72,000
^{210}Pb	5200	7000	5600	n.d.
^{228}Ra	n.d.	n.d.	n.d.	n.d.
^{228}Th	97,000	100,000	126,000	50,000
	W-T-1, <0.1mm	**W-T-2, <0.1mm**	**W-T-3, <0.1mm**	**W-T-4, <0.1mm**
^{238}U	225,000	n.d.	n.d.	67,000
^{226}Ra	200,000	200,000	21,000	136,000
^{210}Pb	2300	5000	2600	2500
^{228}Ra	n.d.	190,000	n.d.	n.d.
^{228}Th	1,031,000	111,000	87,000	70,000
	U-ST-1, <0.1mm	**U-ST-2, <0.1mm**	**U-ST-3, <0.1mm**	**U-ST-4, <0.1mm**
^{238}U	30,300	n.d.	51,500	25,000
^{226}Ra	5300	5600	60,000	19,000
^{210}Pb	n.d.	n.d.	n.d.	1200
^{228}Ra	n.d.	n.d.	n.d.	n.d.
^{228}Th	61,300	61,000	320,000	n.d.
	U-S-5, <2mm	**U-S-6, <2mm**	**U-S-5, <0.1mm**	**U-S-6, <0.1mm**
^{238}U	n.d.	7800	n.d.	27,300
^{226}Ra	18,300	8200	43,000	6400
^{210}Pb	n.d.	n.d.	n.d.	n.d.
^{228}Ra	n.d.	n.d.	145,000	n.d.
^{228}Th	185,000	92,300	230,000	115,000

n.d.: not detected

For this type of leaching test there are no literature data available up to now, therefore a comparison is not enabled.

Many of the phosphate industry's materials do provide high amounts of ^{210}Pb and ^{228}Th for plants, the range is of 67,000-630,000g/m³ for ^{210}Pb and 25,000-340,000g/m³ for ^{228}Th, the ^{226}Ra's transfer factors are around 10,000g/m³.

The bauxite raw materials of the aluminium production show really high TF's for ^{226}Ra (173,000-1,800,000g/m^3) and they are accompanied with some ten thousands of g/m^3 for ^{228}Ra, too. The red sludge waste has much lower transfer factors of 10,000 respectively 30,000g/m^3 for only ^{226}Ra.

The TENORM occurring in frame of the refractory production have generally lower radionuclide transfer factors, mainly lower than 10,000g/m^3. All materials have plant available ^{226}Ra, which comes along with also plant available ^{228}Ra in half of the samples. ^{228}Th is transferable into plants from all type of materials, too, the filter dust waste provides additionally 1800g/m^3 of ^{210}Pb.

The pathway "solid-plant" separates significantly the substances of the crude oil exploitation according to their chemical composition. The muddy sludge samples have very similar TF's for both the radium isotopes of roughly 1000g/m^3, ^{210}Pb and ^{228}Th are of 300g/m^3. In contrast, the scales only release ^{226}Ra (~400g/m^3) beside 800g/m^3 of ^{228}Th in case of W-SC-2.

Many of the investigated radionuclides are mobilisable for plants from the thorium contaminated soils. Especially U-SO-2 and U-SO-3 show mentionable, but undifferentiated transfer factors of some thousands of g/m^3 for almost all radionuclides. U-SO-1 provides 4000g/m^3 of radium beside some few ^{228}Th and U-SO-4 releases more than 60,000g/m^3 of ^{226}Ra.

Apart from ^{228}Ra, the tailings from the uranium mining provide almost all investigated radionuclides, of which ^{226}Ra and ^{228}Th reach the highest dimensions in variations between some ten thousands of g/m^3 and 1,000,000g/m^3. ^{210}Pb is determined for very similar plant transfer factors (2500-7000g/m^3), uranium ranges around 30,000g/m^3. Once again, any grain size influence can be denied. The slags within the dead rocks (U-ST-1 and U-ST-2) have TF's of 5500g/m^3 for ^{226}Ra and 61,000g/m^3 for ^{228}Th. Both the other samples show a very non-uniform radionuclide transfer into plants and also their dimensions differ widely. The sediment samples provide mainly ^{226}Ra and ^{228}Th, from which the uncontaminated sample U-S-5 has the higher transfer factors for both radionuclides without any grain size influence.

7.3 Judgement of the transfer factors obtained

By having a closer look on the transfer factors obtained it becomes clear that there is a wide discrepancy between the radionuclides' leaching behaviour and their dimensions. Apart from the aluminium industry's samples, especially ^{228}Th is omnipresent in the extraction liquids of both pathways, its transfer factors ranging mainly in high dimensions. This might be due to the fact that its progeny ^{208}Tl used for determination by gamma-spectrometry emits a really strong and therefore easily detectable gamma line at 583keV (see chapter "6.2.8 Judgement of the investigation procedures"). So, if ^{208}Tl is once detected in the extraction liquid, but the initial activity concentration of ^{228}Th is only very low, the resulting transfer factor increases rapidly up to some hundred thousand g/m^3 according to the relation given in equation 21. That is the reason for the really high transfer factors calculated for those samples with low ^{228}Th contents

(especially below 200Bq/kg), e.g. the uranium sediments U-S-5 and U-S-6. From those two samples the uncontaminated one (U-S-5) shows even higher transfer factors for both pathways, which are not very realistic. In contrast, the ^{238}U's progeny ^{234}Th being used for the uranium's determination emits just a very weak gamma line in the low energy area of <100keV, which obviously results in rare detection. From the chemical point of view, this is not clear, because both isotopes should show a similar leaching behaviour. This phenomenon is also valid for both the radium isotopes.

The comparison of the transfer factors obtained with some given as reciprocal k_d-values by literature show mostly good agreements, but the intention of each way of calculation differs as mentioned in chapter "7. Leachate prospects". GELLERMANN & SCHULZ (2006) estimated so called "realistic" assumptions (for U, Ra, Pb and Th below 10,000g/m^3) as a result of own DIN 38414-S4 leaching tests for a sandy aquifer in comparison with such TF's being derived from reciprocal k_d-values for sands and they found wide discrepancies between them. Nevertheless, the transfer factors into water for the thorium contaminated soils, which are calculated in the same way in this study and by GELLERMANN & SCHULZ (2006), show a very well correspondence. For that reason, it seems TF's below 10,000g/m^3 are reliable, the other huge ones should be taken more relatively for tendencies.

In further consequences, the investigation procedure as presented in this study seems to be more applicable for highly contaminated samples of some ten thousands of Bq/kg initial activity concentration, whereas materials of lower activity concentrations can be easily taken for releasing very huge and therefore not realistic amounts of radionuclides. This limitation is given by the sensitivity of the gamma-spectrometer system and the extraction volumes (200ml) used respectively the resulting detection limits for the radionuclides (e.g. 0.5Bq/l for ^{226}Ra). As a proposal for the future, it must be emphasised to use larger extraction volumes (and therefore also bigger amounts of starting materials), which then might be reduced by evaporation.

8 Conclusions and outlook

In this thesis, the radiological hazard dimensions of typical TENORM (***T***echnologically ***E***nhanced ***N***aturally ***O***ccurring ***R***adioactive ***M***aterials) are investigated. For that purpose, the chemical types of bounding of the natural radionuclides ^{238}U, ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{228}Th stored in TENORM are analysed by three different extraction procedures (BCR, DIN 19730 and DIN 38414-S4) resulting in 5 fractions: water soluble, easily available, plant available, reducible and oxidisable ones. In order to evaluate the extraction liquids' radionuclide concentrations, a new calibration procedure for the gamma-spectrometer device is introduced. In addition, radon emanation coefficients are determined and radionuclide transfer factors within a production scheme are established. All those parameters are finally rated and used for calculating transfer factors for the pathways "solid-water" and "solid-plant" according to each type of industry.

TENORM samples were delivered from a Romanian aluminium production plant and a Belgian fertiliser industry as well. In Germany, solids were provided by a refractory production plant and crude oil exploitation company, sediments were taken from riversides affected by pit waters from hard coal mining and some soils contaminated especially by ^{232}Th progenies. The obtained data can be summarised by type of industry as follows:

1. Phosphate industry:

The Moroccan raw material phosphate ore is characterised by high concentrations of all the uranium decay series' radionuclides. ^{226}Ra is mostly (50%) bound to organic matter and sulphides, which are the main rock components due to the phosphorite forming by animal particles, whereas the other radionuclides are strongly fixed. The Kola phosphate ore generally contains very low radionuclide concentrations and does therefore not provide mentionable amounts of radionuclides. The strongest enhanced uranium of the produced MN-fertiliser is plant available by 45% and water soluble (30%) as well, which is to be expected for fertiliser. It's high uranium concentration is caused by the phosphoric acid used in frame of the wet production process, because it leaches almost all uranium from the initial rock and transfers it into the product. The waste material phosphogypsum provides almost all the initial lead content for plants. It's generally low activity concentrations can be explained by the unbalanced ratio (5:1) of huge phosphogypsum amounts compared with the produced phosphoric acid volume. If the raw materials contain enhanced radionuclide concentrations, significant radon emanation rates can occur and also the produced fertiliser are proven to emanate some radon. The calculated transfer factors mainly concern ^{226}Ra into plants for all materials involved, the other ones must be classified as unrealistic high, especially that of the phosphogypsum's ^{210}Pb into plants.

2. Aluminium production:

Both the bauxite raw materials contain enhanced ^{238}U and progeny concentrations and show comparable leaching behaviours, especially the Brazilian Trombeta bauxite provides ^{226}Ra and ^{210}Pb for the easily exchangeable fraction by 55% respectively 20%. In addition, ^{226}Ra is also determined to be available for plants by 40%. 40% of ^{226}Ra are both water soluble and also easily

exchangeable from the red sludge waste produced in the aluminium plant Tulcea, Romania. Due to the relatively low initial activity concentrations in that substance, the radionuclide transfer from the raw materials seems to be diluted during the aluminium production process. Significant radon emanation rates are observed for the Trombeta bauxite. According to the transfer factors, both the bauxite ores can contribute to a ^{226}Ra pollution in water, in case of the pathway "solid-plant" attention is to be paid for ^{228}Ra.

3. Refractory industry:

Zircon sand is used as an additive in frame of producing refractory materials such as fused zirconia mullite (FZM). From the raw material just low amounts of ^{226}Ra are totally solved (10%) due to the radionuclides' strong fixation in the zircon's crystal lattice, other radionuclides are not mentionably leached from any of the investigated substances. Concerning the products FZM, up to 20% of the initial ^{226}Ra is bound to the oxidisable fraction, just very few amounts are proven to be easily available. Since the fusion process raises temperatures where ^{210}Pb (beside ^{222}Rn and ^{210}Po) is removed from the production succession, the generated filter dust waste is highly contaminated by ^{210}Pb concentrations of more than 160,000 Bq/kg, from which 10% are bound to iron and manganese oxides and 30% are fixed on sulphides. All materials are attributed by rather low radon emanation rates as a consequence of the ^{226}Ra's firm type of bounding. The transfer factors show same leaching potentials for ^{228}Th by water and for plants, the latter can also be endangered by both radium isotopes.

4. Crude oil exploitation:

The sludge and scale wastes from the crude oil exploitation are especially contaminated by ^{210}Pb, ^{226}Ra is also relevant for the sludge samples (both 45,000Bq/kg roughly). All the ^{210}Pb concentration contained in the scale is completely leached in frame of the BCR procedure, 65% are easily exchangeable, 10% are bound to iron and manganese oxides and 25% are fixed on organic matter and sulphides. The sludge samples are determined for similar initial ^{210}Pb and also ^{226}Ra concentrations, but the most of them is left in the residual. 18% of lead are easily exchangeable, 6% are fixed in the reducible fraction and 18% in the oxidisable one. The mentioned ^{226}Ra is only detected in the oxidisable fraction by 3%. The sludge samples are proven to emanate high amounts of radon (up to 570Bq/kg) due to the presence of an oil-water mixture in the materials, the scales' emanation rates are much lower as a result of the ^{226}Ra's strong fixing as radiobarite [Ba(Ra)SO_4]. The sludge can release both radium isotopes and ^{228}Th as well for water, the plant transfer is mainly affected by ^{228}Th.

5. Hard coal mining:

As a result of the pit waters' discharge into rivers, sediments got contaminated by ^{226}Ra and its growing again progeny ^{210}Pb. But all samples are determined not to provide one of the enriched ^{226}Ra and lead radionuclides under any of the investigated chemical conditions. This can be explained by the very stable crystalline structure of the radiobarite [Ba(Ra)SO_4] they are fixed in, so that solutions used are not sufficiently aggressive to disrupt and remove compounds. The very well corresponding amounts of ^{228}Th present in all the three BCR fractions of all sediments can be neglected due to very low initial activity concentrations (<200 Bq/kg).

6. Thorium contaminated soils:

The by far highest activity concentrations are found in the thorium bearing soils. At the one location, residues of thorium-cobalt catalysts, which had formerly been used in frame of the so-called FISCHER-TROPSCH synthesis for producing synthetic fuels by hydrogenation of coal, were disposed but meanwhile removed. The second site got contaminated by thorium bearing dust when a thorium processing gas mantle plant had been destroyed by an air-raid at the end of the Second World War and the dust was widely spread on the factory's vicinity. The low leaching coefficients for ^{228}Ra and ^{228}Th of soil 1 being derived from the first location are put into perspective by their extremely high initial concentrations, so 2% each are fixed in the reducible fraction and 8% in the oxidisable one, 2% of ^{228}Ra are also plant available. In soil 2 from the second site, roughly 20% of ^{228}Ra can be found in each of the BCR fractions and 8% are plant available, 12% of ^{228}Th are easily exchangeable and reducible respectively, 25% are bound to organic matter and sulphides. Soil 3, taken at the same site, shows similar radionuclides' types of bounding, just the initial activity concentrations, which are also of same ratios, are slightly lower. Despite a slightly enhanced effective dose, the fourth soil sample does not contain high radionuclide concentrations. Due to the omnipresence of ^{232}Th progenies, radon emanation coefficients are not determined. The ^{232}Th progenies are calculated to be transferable into water only in very few amounts, in contrast the pathway "solid-plant" is a very important one for almost all investigated radionuclides (some thousands of g/m^3).

7. Uranium industry:

Of course, the used uranium ores contain high activity concentrations of ^{238}U and progenies (up to 900,000Bq/kg). These radionuclides do not show a preferred type of bounding, they are present in all the BCR's extraction fractions in high volumes but not proven to be water or plant available. The tailing wastes are characterised by unbalanced radionuclide ratios increasing downwards the uranium decay series, which is to be explained by some co-leaching in frame of extracting the uranium. Huge portions (up to 30%) of their contained ^{226}Ra and ^{210}Pb are easily available, the first one is also widely plant available. The unwanted by-products show deviating leaching behaviours due to their different rock types. Slags just provide low amounts of radionuclides, whereas the dead rocks contain the uranium decay series' radionuclides mostly bound to sulphides beside some portions being bound to grain surfaces. Sediments along rivers crossing such a mining area are proven to be significantly contaminated, but the very most of the radionuclides is strongly fixed similar to those of the hard coal mining. The uranium ores and the tailings as well do emanate radon in high rates, those of the dead rocks are much lower. Contaminated sediments can show some emanating radon, which depends on their position in relation to the river's waterline. Both the uranium ores and the tailings cause a strongly enhanced radiological risk, the first ones as a consequence of their immense activity concentrations and the latter by their easily mobilisable radionuclides and high radon emanation rates as well. The tailings' show a ^{226}Ra transfer in to water, whereas the pathway "solid-plant" is affected by uranium and lead, the other calculated transfer factors are of unrealistic dimensions. In case of the dead rocks and also the sediments, some reliable volumes of ^{226}Ra are transferable into plants. The other presented transfer factors seem to be too high for a realistic leaching behaviour.

8. Investigation procedure:

As the analyses show, the developed measuring procedure for the gamma-spectrometry is reliable and leads to comparable and reproducible results, i.e. samples from same sources are determined for same radionuclides' types of bounding. This is proven by all the extraction liquids of the four sediments from hard coal mining influenced environment and the leaching coefficients of the highly thorium contaminated soils 2 and 3 as well. All the other samples differ either in their source or kind of material, so a comparison is not enabled. In addition, the influence of different grain sizes on the radionuclides' leaching behaviour is investigated on the basis of the samples from aluminium production and uranium tailings as well. It can be stated that this parameter just slightly influences the radionuclides' availablity, the milled substances provide only some few portions more due to enhanced specific grain surfaces, but sometimes the opposite is observed, too. A limit of the applied scientific extraction procedures is given by uranium oxide bearing hard rocks, from which no detectable portions are leached. No surprise, the uranium industry is forced to use strong reagents such as sulphuric acid for mobilising that radionuclide. In contrast, ^{228}Th is omnipresent in almost all extraction liquids, because it can be detected very easily by gamma-spectrometer due its strongly emitted gamma line at 583keV (almost 85%). Nevertheless, also ^{234}Th from the ^{238}U decay should be leached in similar dimensions as the ^{228}Th is as a result of same chemical properties, but very often this radionuclide is not detectable. The same is valid for the radium isotopes in some extent. This might be due to its weakly emitted gamma line in the low energy area (4.1% at 63keV) on the one hand, on the other the relatively small amount of solid starting material for the extraction procedures can be taken for interfering. This seems to be a limitation of the investigation procedure as presented in this study, which is based on the original extraction procedures' instructions for heavy metals.

Nevertheless, the obtained results clearly show that there is not only a need to keep TENORM under control for their initial activity concentrations, radon releases and effective doses, but for their radionuclide mobilisation potential and resulting environmental influences, too.

Outlook:

Since it was not possible to get some samples from the titanium processing industry and waterworks as well, these types of TENORM industries should be put in the focus for investigating the radionuclides' types of bounding in those materials involved. Another proposal is to carry out in-situ radon exhalation measurements where the TENORM occur, which would result in reliable statements about the radon hazard potential for that specific processing plant. But this is not possible without the industry's support (i.e. giving access) or a legislative enforcement. Concerning the developed investigation procedure, the author proposes to use bigger amounts of starting materials for the extraction procedures resulting in larger extraction volumes, which then might be reduced by evaporation. By doing so, the radionuclides' activity concentrations in the extraction liquids will increase and the detection limits decrease.

9 References

ABDULLAH, W. A-S. & DAHL, R. (1995): Determination of thorium and uranium in nitrophosphate fertilizer solution by ion chromatography. – Journal of Chromatography A, **706**, p. 175-181.

AAC (2006): http://www.aluminium.org.au/npi/Rep1_Page3.htm. – Official homepage of the Australian Aluminium Council (AAC), Canberra, Australia.

BAHLBURG, H. & BREITKREUZ, C. (1998): Grundlagen der Geologie. – 1. Aufl., 328 S.; Ferdinand Enke Verlag, Stuttgart.

BARTHEL R., GOLDAMMER W., HAKE W. & KUGELER E. (2000): Eingrenzung und Bewertung der von den vorgesehenen NORM-Regelungen der Novelle StrlSchV betroffenen Bereiche. – Erstellt durch BRENK-Systemplanung, BS-Bearb. Nr. 9410/2, 93 S.; Aachen.

BAUMBACH, G. (2005): Luftreinhaltung - Entstehung, Ausbreitung und Wirkung von Luftverunreinigungen, Meßtechnik, Emissionsminderung und Vorschriften. – 15. Aufl., 461 S.; Springer-Verlag, Berlin.

BECKER, D.E., MUGRAUER, O. & LEHMANN, K.-H. (1992): Strahlenexposition durch den Umgang mit Reststoffen der Kohleverbrennung. – Abschlußbericht über das Forschungsvorhaben StSch. 1132.

BEGUS, T. (1989): Hidrogeoloske raziskave na RUZV. – Unpublished report (in Slovenian), RUZV, Gorenja Vas, Slovenia.

BEGUS, T., BUSER, I., CADEZ, F. & VIDMAR, S. (1996): Landslide stabilisation of a mill tailing disposal by a drainage tunnel at the uranium mine Zirovski vrh, Slovenia. – In: SENNESET, K. (1996): Proceedings of the seventh international symposium on landslides held in Trondheim, Norway, 17.-21. June 1996, Proceedings published by Balkema, Rotterdam, Netherlands.

BELEITES, M. (1992): Altlast Wismut. – 97 S.; Brandes & Apsel Verlag, Frankfurt am Main.

BELL, J. & BATES, T.H. (1988): Distribution coefficients of radionuclides between soils and groundwaters and their dependence on various parameters. – The Science of the Total Environment, **69**, p. 297-317.

BBODSCHV (1999): Bundesbodenschutz- und Altlastenverordnung (BBodSchV) BGBl. I, 1554.

BMU (2000): Umweltradioaktivität und Strahlenbelastung. – Jahresbericht 1998. – Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit (BMU), 268 S., Bonn.

BR (2004): Umweltradioaktivität und Strahlenbelastung im Jahr 2004. – Unterrichtung durch die Bundesregierung, Berlin.

BORSCH, P., FEINENDEGEN, L. E., FELDMANN, A., MÜNCH, E. & PASCHKE, M. (1996): Radioaktivität und Gesundheit. – 224 S., Bayerisches Staatsministerium für Landesentwicklung und Umweltfragen, München.

BRADLEY, F.J. (2003): NCRP Report No. 139, Risk-Based Classification of Radioactive and Hazardous Chemical Wastes. – Health Physics, **85** (6), p. 759-760.

BUE (2006): http://www.bergbau-und-energie.de/images/kohlekraftwerk.gif. – Official homepage of the German mining and energy industry (Bergbau und Energie, BUE).

CADEZ, F., LIKAR, B., LOGAR, Z. & GANTAR, I. (2002): Mining Impact on Ground Water of Uranium Mine Zirovski Vrh. – Unpublished report, Institute for Mining Technology and Environment (IRGO), Ljubljana, Slovenia.

CHALUPNIK, S., MICHALIK, B., WYSOCKA, M., SKUBACZ, K. & MIELNIKOW, A. (2001): Contamination of settling ponds and rivers as a result of discharge of radium-beraring waters from Polish coal mines. – Journal of Environmental Radioactivity, **54**, p. 85-98.

CHALUPNIK, S. & AGUADO, J. (2005): Radium leaching from mine deposits and other materials. – In: International Symposium on Naturally Occurring Radioactive Materials (NORM IV) held in Szczyrk, Poland, 17.-21. May 2004, Proceedings published by IAEA, Vienna, Austria.

CHEM (2006): http://www.chemistryworld.de/cheminfo/2509-lex.htm. – Online-Chemikalienlexikon: Aluminium.

CHRISTEN, H.R. (1976): Organische Chemie - Struktur, Stoff, Reaktion. – 266 S.; Otto Salle Verlag, Frankfurt am Main.

CRPC (2000): Canadian guidelines for the management of naturally occurring radioactive materials (NORM). – 1st edition; Canadian NORM working group of the federal provincial territorial Radiation Protection Committee (CRPC), published by authority of the Minister of Health.

CTUL (2006): http://www.primaria-tulcea.ro/en/index.php?p=alum. – Official homepage of the city Tulcea, Romania.

CULLEN, T.L. & PENNA FRANCA, E. (1977): Proceedings of International Symposium on High Natural Radioactivity, Pocos de Caldas, Brazil 16.-20. June 1975. – Academia Brasileria de Ciencias, Rj.

CUTSHALL, N.H., LARSEN, I.L. & OLSEN C.R. (1983): Direct analysis of ^{210}Pb in sedimental samples: Self-absorption corrections. – Nuclear Instruments and Methods, **206**, p. 309-312.

DAHLKAMP, F.J. (1993): Uranium ore deposits. – 460 S.; Springer-Verlag, Berlin.

DALHEIMER, A. & HENRICHS, K. (1994): Monitoring of workers occupationally exposed to thorium in Germany. – Radiation Protection Dosimetry, Vol. **53**, Nos. 1-4, p. 207-209.

DAVIDOVITS, J. (1988): First European Conference on soft Mineralurgy, Proceedings Geopolymer '88. Geopolymer Chemistry and Properties, Vol. **1**, p. 25-48.

DEW (2006): www.erdoelmuseum.de. – Official homepage of "Deutsches Erdölmuseum Wietze" (DEW), Wietze, Germany.

DIN 38404 C16 (1989): Bestimmung von Radionukliden in Schlamm, Sediment und Schwebstoff mittels Gammaspektrometrie. – Beuth-Verlag, Berlin.

DIN 38414 S4 (1984): Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Schlamm, und Sedimente (Gruppe S); Bestimmung der Eluierbarkeit mit Wasser (S4). – Beuth-Verlag, Berlin.

DIN 38414, Teil 16 (1988): Bestimmung von Radionukliden in Trink-, Grund-, Oberflächen- und Abwasser mittels Gammaspektrometrie. – Beuth-Verlag, Berlin.

DIN 19730 (1997): Bodenbeschaffenheit - Extraktion von Spurenelementen mit Ammoniumnitrat. – Beuth-Verlag, Berlin.

DYBEK, J. (1962): Zur Geochemie und Lagerstättenkunde des Urans. – 163 S.; Verlag Gebr. Bornträger, Berlin-Nikolassee.

ECRR (2003): Criteria for "clearance": controlling the release of solid materials of very low average activity for reuse, recycling and disposal. – Guidance note no. 2003/1; European Committee on Radiation Risk (ECRR), Brussels.

EFMA (1997): http://www.efma.org/introduction/section02.asp. – Official homepage of the European Fertilizer Manufacturers Association (EFMA), Brussels, Belgium.

EISNER, W., FLADT, R., GIETZ, P., JUSTUS, A., LAITENBERGER, K. & SCHIERLE, W. (1986): Elemente Chemie. – 1. Aufl., 224 S.; Ernst Klett Verlag, Stuttgart.

ELSTER, J. & GEITEL, H. (1904): Über die radioaktive Substanz, deren Emanation in der Bodenluft und der Atmosphäre enthalten ist. – Phys. Z., **5**, 1, S. 11-20.

EDMONSON, R. M., JELIFFE, M. R. & HOLWAND, K. N. (1997): Naturally Occurring Radioactive Material (NORM) - A Primer. – 16 E. Min. L. Inst., chapter 2; Jackson, Mississippi, USA.

EPA (2000): Evaluation of EPA's Guidelines for Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM). – Report to Congress; US Environmental Protection Agency (EPA), 402-R-00-01.

EU COUNCIL DIRECTIVE 96/29/EURATOM (1996): Basic Safety Standards (BSS) for the protection of the health of workers and the general public against the dangers arising from ionising radiation. – Directive from 13th May 1996, 182 p.; Brussels.

EU COUNCIL DIRECTIVE 97/43/EURATOM (1997): Health protection of persons against hazards resulting from ionising radiation occurring as medical exposition. – Directive from 30th July 1997, 9 p.; Brussels.

FALBE, J. & REGITZ, M. (1995): ROEMPP-Chemielexikon. – 9. Aufl., Band 1 A-Cl; Thieme Verlag, Stuttgart.

FEIGE, S. (1997): Radionuklid-Kontamination von Wässern, Sedimenten und Böden durch den Steinkohle- und Braunkohlebergbau. – 147 S., Diploma thesis, University of Essen.

FEIGE, S. & WIEGAND, J. (1999): The influence of coal mining on radon potential. – Il nuovo cimento, **22** (3-4), p. 345-352.

FELDHEIM, W., TAUBE, M. & HEEPE, R. (1995): Ermittlung und Beräumung thoriumkontaminierter Flächen auf dem Betriebsgelände der BASF Schwarzheide GmbH. – In: Landesumweltamt Brandenburg - Berichte aus der Arbeit 1994.

FIESER, L.F. & FIESER, M. (1954): Lehrbuch der organischen Chemie. – 1244 S.; Verlag Chemie GmbH, Weinheim/Bergstr.

FIPR (1998): Evaluation of exposure to technologically enhanced naturally occurring radioactive materials (TENORM) in the phosphate industry. – Final report, Publication No. 05-046-155, 270p., Florida Institute of Phosphate Research (FIPR), Bartow, Florida.

FISCHER, F. & MEYER, K. (1931): Über die Verwendbarkeit von Nickelkatalysatoren für die Benzinsynthese. – Brennstoff-Chem. **12**, 225, S. 534.

FUNKE, L. & SCHULZ, H. (1999): Empfehlung zur Optimierung der Messung der spezifischen Aktivitäten natürlicher Strahler in „NORM"-Stoffen. – Report in frame of revising the German Radiation Protection Ordinance (StrSchV), IAF Radioökologie GmbH, Dresden.

GANS, I., FUSBAN, K., WELLER, E. & WOLLENHAUPT, H. (1982): Radium in waste water from coal mines and other sources in the Federal Republic of Germany. – Natural Radiation Environment, p. 444-451, Wilay Eastern Ltd., New Delhi.

GATZWEILER, R. (1996): Lagerstätten- und produktionsbedingte Umweltauswirkungen des Uranbergbaus. – In: SIEHL, A. (1996): Umweltradioaktivität. – 411S.; Ernst & Sohn Verlag, Berlin.

GATZWEILER, R. & KEGEL, K.-E. (1989): Der Energierohstoff Uran. – Die Geowissenschaften, **7**, S. 313-323.

GDA (2002): Informationen über den Werkstoff Aluminium. – Gesamtverband der Aluminiumindustrie (GdA), Düsseldorf.

GEI (2006): http://www.energiewelten.de/elexikon/lexikon/seiten/htm/020703_Urangewinnung.htm. – Official homepage of the German Electricity Industry (GEI), Frankfurt am Main.

GELLERMANN, R., SCHULZ, H. & KÜPPERS, C. (2003): Mengenaufkommen an NORM-Rückständen für das deutsche Entsorgungskonzept. – Abschlußbericht zum Vorhaben SR 2416 des Bundesamtes für Strahlenschutz, 220 S.; Magdeburg, Dresden und Darmstadt.

GELLERMANN, R. & SCHULZ, H. (2006): Methodische Weiterentwicklung des Leitfadens zur radiologischen Untersuchung und Bewertung bergbaulicher Altlasten und Erweiterung des Anwendungsbereichs, Teil B: Erweiterung des Anwendungsbereichs auf NORM-Rückstände. – Abschlußbericht zum Vorhaben StSch 4416, 163 S.; Magdeburg und Dresden.

GEORGESCU, D., AURELIAN, F., POPESCU, M. & RADULESCU, C. (2005): Sources of TENORM – Inventory of phosphate fertilizer and aluminium industry. – In: International Symposium on Naturally Occurring Radioactive Materials (NORM IV) held in Szczyrk, Poland, 17.-21. May 2004, Proceedings published by IAEA, Vienna, Austria.

GESELL, TH.F. (1975): Occupational Radiation Exposure due to ^{222}Rn in Natural Gas and Natural Gas Products. – Health Physics, **29** (5), p. 681-687.

GLE (2006): http://earth.google.de. – GOOGLE-Earth, 12. June 2006 - Google Earth (Version 4 - BETA).

GMR (2007): http://www.quecksilber-gmr.de/gbverfahren. – Official homepage of the "Gesellschaft fuer Metallrecycling mbH" (GMR), Leipzig.

GODOY, J.M. & PETINATTI DA CRUZ, R. (2003): ^{226}Ra and ^{228}Ra in scale and sludge samples and their correlation with the chemical composition. – Journal of Environmental Radioactivity, **70**, p. 199-206.

GODOY, J.M., CARVALHO, F., CORDILHA, A., MATTA, E.M. & GODOY, M.L. (2005): ^{210}Pb content in natural gas pipeline residues ("black-powder") and its correlation with the chemical composition. – Journal of Environmental Radioactivity, **83**, p. 101-111.

GOR (2004): Implementation plan for Directive 1999/31/ec on the landfill of waste. – Government of Romania (GoR), October 2004.

GRAUBNER, R. (1980): Lexikon der Geologie, Minerale und Gesteine. – 1. Aufl., 463 S.; Vollmer Verlag, München.

GRAY, P. (1990): Radioactive materials could pose problems for the gas industry. – Oil and Gas Journal, **45** e.

GRAY, P. (1993): Norm contamination in the petroleum industry. – Journal of Petroleum Technology, **45**, 12 e.

GUO Q., CHENG J., SHANG B. & SUN J. (2001): The level of indoor thoron and its progeny in four areas in China. – J. Nucl. Sci. Technol. **38**, No. 9, p. 799-803.

HARTOG, F.A., KNAEPEN, W.A.I., JONKERS, G., (1998): Origin and encounter of Pb-210 in E&P facilities. – In: Proceedings of 2nd NORM Symposium, Krefeld, p. 53-57.

HEATON, B. & LAMBLEY, J. (1995): TENORM in the Oil, Gas and Mineral Mining Industry. – Appl. Radiat. Isot., **46**, No. 6-7, p. 577-581.

HENNINGSEN, D. & KATZUNG, G. (1998): Einführung in die Geologie Deutschlands. – 5. Aufl., 244 S.; Enke-Verlag, Stuttgart.

HGN (2001): Ableitung von Prüfwerten für die Beurteilung einer Grundwassergefährdung durch natürlich radioaktive Altlasten im Gebiet der Stadt Oranienburg. – HGN Hydrogeologie GmbH.

HIMSTEDT, F. (1904): Über die radioaktive Emanation der Wasser und Ölquellen. – Phys. Zs., **5**, S. 210-213.

HYRSL, J. (1992): Mineralien, Geologie und Bergbaugeschichte von Pribram, Böhmen. – 64 S.; Doris Bode Verlag, Haltern.

IAEA (2005): International Symposium on Naturally occurring radioactive materials (NORM IV) held in Szczyrk, Poland, 17.-21. May 2004, Proceedings published by IAEA, Vienna, Austria.

JANSSEN, A. (1984): Study of the radiation protection problem caused by the presence of 226-Ra in building materials. – Proceedings of the Sixth International Congress of the International Radiation Protection Association held in Berlin (West), 7.-12. May 1984, Germany.

JUHASZ, L. & SZERBIN, P. (2002): Sources of TENORM - Inventory of industries, materials or residues. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Hungarian Deliverable No. 1, 16 p., Budapest.

VAN KAUWENBERGH, S.J. (1997): Cadmium and other minor elements in world resources of phosphate rock. – Proceedings No. 400, The Fertilizer Society, London.

KEMSKI, J., KLINGEL, R. & SIEHL, A. (1996): Die terrestrische Strahlung durch natürlich radioaktive Elemente in Gesteinen und Böden. – In: SIEHL, A. (1996): Umweltradioaktivität. – 411S.; Ernst & Sohn Verlag, Berlin.

KGS (2006a): http://www.uky.edu/KGS/coal.htm. – Official homepage of the Kentucky Geological Survey (KGS), USA.

KGS (2006b): http://www.uky.edu/KGS/coal/uses_of_coal.htm. – Official homepage of the Kentucky Geological Survey (KGS), USA.

KINDER, H. & HILGEMANN, W. (2001): dtv-Atlas Weltgeschichte - von den Anfängen bis zur Gegenwart. – 2. Aufl., 631 S.; Deutscher Taschenbuch Verlag, München.

KNAEPEN, W.A.I., BERGWERF, W., LANCÉE, P.J.F., VAN DIJK, W., JANSEN, J.F.W., JANNSSEN, R.G.C., KIETZENBERG, W.H.T., VAN SLUIJS, R., TIJSMANS, M.H., VOLJERS, K.J. & VOORS, P.I. (1995): State-of-the-art of NORM nuclide determination in samples from oil and gas production: validation of potential standardization methods through an interlaboratory test program. – Journal of Radioanalytical and Nuclear Chemistry Articles; Vol. **198**, No. 2, p. 323-341.

KMC (2005): http://www.kyanite.com/mullite.html. – Official homepage of the Kyanite Mining Corporation (KMC), Virginia, USA.

KOLB, W. & WOJCIK, M. (1985): Enhanced radioactivity due to natural oil and gas production and related radiological problems. – The Science of the Total Environment, **45**, p. 77-84.

KRIZMAN, M. & STEGNAR, P. (1992): Environmental impact of the "Zirovski Vrh" uranium mine on the enhancement of outdoor radon concentrations. – Radiation Protection Dosimetry, **45**, No. 1/4, p. 723-728.

KRIZMAN, M., BYRNE, A.R. & BENEDIK, L. (1995): Distribution of ^{230}Th in milling wastes from the Zirovski vrh uranium mine (Slovenia), and its radioecological implications. – Journal of Environmental Radioactivity, **26**, p. 223-235.

KRUEGER, J. (1999): Studie über Anfall und Verbleib radioaktiver Rückstände im Bereich der Eisen- und Nichteisenmetallurgie. – Erstellt am Institut und Lehrstuhl für metallurgische Prozesstechnik und Metallrecycling der RWTH Aachen, 31 S.; Aachen.

LACIOK, A., MORAVANSKA, H. & VOJTECH, O. (2002): Inventory of the Czech industries using NORM (TENORM). – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Czech Deliverable No. 1, 49 p., Prague.

LANDROCK, K. (2002): Verwendung von Thorium in optischen und optoelektrischen Linsen - nach wie vor nicht unproblematisch. – 23. Sitzung AK NAT, Wernigerode, Mai 2002.

LARUE, J., WEISS, D. & KIESSIG, G. (2002): Methods for storage and disposal of residues from waste-water treatment of former uranium mining and milling facilities in Germany. – In: International Symposium on Technologically Enhanced Natural Radiation (TENR II) held in Rio de Janeiro, Brazil, 12.-17. September 1999, Proceedings published by IAEA, Vienna, Austria.

LEOPOLD, K. & WIEGAND, J. (2002): Identification of sources, levels and inventory of TENORM. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Deliverable No. 15, 21p., University Duisburg-Essen.

LEOPOLD, K., PETERS, B., WEISS, D. & WIEGAND, J. (2002): German national report to levels and inventory of TENORM. – TENORMHARM-project (contract No. FIGM-CT-2001-00174), Deliverable 1, 49 p., Essen/Berlin.

LEOPOLD, K., MICHALIK, B. & WIEGAND, J. (2007): Availability of radium isotopes and heavy metals from scales and tailings of Polish hard coal mining. – Journal of Environmental Radioactivity, **94**, p. 137-150.

LINEG (1995): Jahresbericht 1995 der Linksniederrheinischen Entwässerungs-Genossenschaft. – 119 S., Linksniederrheinische Entwässerungs-Genossenschaft (LINEG), Kamp-Lintfort.

LOWE LEO, M. (1992): Radiological implications of naturally occurring radioactivity in an elemental phosphorus refinery. – Proceedings of the 8th International Congress of the International Radiation Protection Association, held on 17-22 May 1992, Montreal, Canada.

DE LUCA, M. (1999): International report. – Offshore, **6** (5), p. 38-50, p. 168-77.

LUCAS, H.F. (1957): Improved low-level alpha-scintillation counter for radon. – Rev. Sci. Instrum., **28**, p. 680-683; New York.

MARTIN, A., MEAD, S. & WADE, B. O. (1997): Materials containing natural radionuclides in enhanced concentrations. – EUR 17625.

MARTIN, R., SANCHEZ, D.M., GUTIERREZ, A.M., (1998): Sequential extraction of U, Th, Ce, La and some heavy metals in sediments from Ortigas river, Spain. – Talanta, **46**, p. 1115-1121.

MATTHES, S. (1996): Mineralogie. – 5. Aufl., 499 S.; Springer-Verlag, Berlin.

MERKEL, B. & DUDEL, G. (1998): Untersuchungen zur radiologischen Emission des Uran-Tailings Schneckenstein. – Studie für das Sächsische Staatsministerium für Umwelt und Landesentwicklung, Dresden; 198 S., Freiberg/Dresden.

MICHALIK, B. (2002): Identification of sources, levels and inventory of TENORM. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Polish Deliverable No. 1, 28 p., Katowice.

MICHALIK, B. (2005): 2.2. Compilation and ranking of exposure to workers and members of the public by type of industry. – EU-project TENORMHARM (contract No. FIGM-CT-2001-00174), Deliverable No. 5, Comparison and summary of national reports by Polish Central Mining Institute (GIG), 11 p., Katowice.

MOFFETT, D. (1977): The disposal of solid wastes and liquid effluents from the milling of uranium ores. – CANMET report, 76-19, Ottawa, Canada.

MÜLLER, G. (1977): Torf - Braunkohle - Steinkohle. – In: FÜCHTBAUER, H. & MÜLLER, G.: Sedimente und Sedimentgesteine, Teil II. – 3. Aufl., 782 S.; Schweizerbart'sche Buchhandlung, Stuttgart.

MLUV (2002): Umweltdaten aus Brandenburg - Bericht 2002. – 208 S., Ministerium für Ländliche Entwicklung, Umwelt und Verbraucherschutz (MLUV), Potsdam.

MLUV (2005): 10 Jahre Altlastensanierung im Rahmen der Haftungsfreistellung der BASF Schwarzheide (29.06.2005). – http://www.mluv.brandenburg.de/cms/detail.php/5lbm1.c. 98726.de, official homepage of the Ministerium für Ländliche Entwicklung, Umwelt und Verbraucherschutz (MLUV), Potsdam.

MURRAY, A. S., MARTEN, R., JOHNSTON, A. & MARTIN, P. (1987): Analysis for naturally occurring radionuclides at environmental concentrations by gamma spectrometry. – Journal of Radioanalytical and Nuclear Chemistry, Vol. **115**, 2, p. 263-288.

NAGEL, G. (2002): Atomversuche in Deutschland - Geheime Uranarbeiten in Gottow, Oranienburg und Stadtilm. – 2. Aufl., 336 S.; Heinrich-Jung-Verlagsgesellschaft mbH, Zella-Mehlis/Meiningen.

NAS (National Academy of Sciences) (1988): Health risks of radon and other internally deposited alpha emitters. – BEIR IV National Research Council, Washington DC: Academy Press.

NICKEL, E. (1980): Grundwissen in Mineralogie. – 3. Aufl., 220 S.; Ott Verlag Thun, Schweiz.

NLFB (2002): http://www.bgr.de/n306/ jahresbericht_2001.pdf. – Official annual report 2001 by the Geological Survey of Lower Saxony (Niedersächsisches Landesamt für Bodenforschung, NLfB), Hannover.

ORTEC (2002): InterWinner 5.0 - MCA Emulation, data acquisition and analysis software for gamma and alpha spectroscopy. – Software user's manual, IW-B32.

PASCHOA, A.S. & GODOY, J.M. (2002): The areas of high natural radioactivity and TENORM wastes. – International Congress Series 1225, p. 3-8.

PENFOLD, J. S. S., DEGRANGE, J.-P., MOBBS, S. F. & SCHNEIDER, T. (1999): Establishment of reference levels for regulatory control of workplaces where materials are processed which contain enhanced levels of naturally-occurring radionuclides. – Radiation Protection 107, European Commission, Luxembourg.

VON PHILIPSBORN, H. (1998): Strahlenschutz: Radioaktivität und Strahlungsmessung. – 6. Aufl., 218 S.; Bayrisches Staatsministerium für Landesentwicklung und Umweltfragen, München.

PIERCE, A.P., MYTTON, J.W. & GOTT, G.B. (1955): Radioactive Elements and their Daughter Products in the Texas Panhandle and other Gas Fields in the U.S.A. – Proc. 1st Int. Conf. Peaceful uses of Atomic Energy, Pergammon Press, Geneva.

PINDER, D. (2001): Offshore oil and gas: global resource knowledge and technological change. – Ocean & Coastal Management, **44**, p. 579-600.

POFFIJN, A. (2002): Sources of TENORM - Inventory of industries, materials or residues. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Belgian Deliverable No. 1, 11 p., Brussels.

POFFIJN, A. & DE CLERK, T. (2004): Compilation and ranking of exposure to workers and members of the public by type of industry. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Belgian Deliverable No. 5, 6 p., Brussels.

POFFIJN, A. & WEISS, D. (2005): Harmonisation of legislation. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Final report on work package 3, 8 p., Brussels/Berlin.

RADULESCU, C. & POPESCU, M. (2002a): Sources of TENORM - Inventory of industries, materials or residues. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Romanian Deliverable No. 1, 75 p., Bucharest.

RADULESCU, C. & POPESCU, M. (2002b): Assessment of effective additional dose for the population from critical group in bauxite processing activity. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Romanian Deliverable No. 2, 23 p., Bucharest.

RADULESCU, C. & POPESCU, M. (2005): Guidance of measures directed towards mitigation of harm & Guidance for remedial actions by type of industry. – EU-Project TENORMHARM (contract No. FIGM-CT-2001-00174), Romanian Deliverable No. 8 and 11, 2 p., Bucharest.

RAMA & MOORE, W.S. (1984): Mechanism of transport of U - Th series radioisotopes from solids into water. – Geochim. Cosmochim. Acta, **48**, 2, p. 395-399.

RICHTER, D. (1992): Allgemeine Geologie. – 4. Aufl., 349 S.; Walter de Gruyter Verlag, Berlin.

RIEDEL, E. (1994): Anorganische Chemie. – 3. Aufl., 921 S.; Walter de Gruyter Verlag, Berlin.

ROECK, D.R., REAVEY, T.C. & HARDIN, J.M. (1987): Partitioning of natural radionuclides in the waste streams of coal-fired utilities. – Health physics, **52** (3), p. 311-323.

ROJC, J. & JOVANOVIC, P. (2005): Test of the material for radon seal layer at the mine waste disposal site Jazbec. – In: International Symposium on Naturally Occurring Radioactive Materials (NORM IV) held in Szczyrk, Poland, 17.-21. May 2004, Proceedings published by IAEA, Vienna, Austria.

RÖNSCH, W. (1996): Radioaktive Umweltkontamination durch den Bergbau in Deutschland. – In: SIEHL, A. (1996): Umweltradioaktivität. – 411S.; Ernst & Sohn Verlag, Berlin.

ROSENBAUM-MERTENS, J. (2003): Seesedimente als Schadstoffarchive - Veränderungen im Schwermetalleintrag in die Umwelt seit 1945. – PhD-thesis, 192 p., University Duisburg-Essen.

RP 88 (1997): Recommendations for the implementation of Title VII of the European Basic Safety Standards Directive (BSS) concerning the significant increase in exposure due to natural radiation sources. – Radiation Protection 88, European Commission, Luxembourg.

RP 95 (1999): Reference levels for workplaces processing materials with enhanced levels of naturally occuring radionuclides. – Radiation Protection 95, European Commission, Luxembourg.

RUCKERBAUER, F., DIETL, F. & WINKLER, R. (1997): Das zentrale Gammaspektrometrie-Labor des GSF-Instituts für Strahlenschutz. – GSF-Bericht 5/97, 31 S., GSF - Forschungszentrum für Umwelt und Gesundheit GmbH, Neuherberg.

SALDAN, M. (1965): Biuletyn Instytutu Geologicznego, Warszawa, Poland, Vol. **5** (in Polish).

SCHKADE, U.-K., BEYERMANN, M., HARTMANN, M., NAUMANN, M., SEEHAFER, M., ULLMANN, W., WILL, W. & WINKELMANN, I. (1999): Verfahren zur Bestimmung von natürlichen Radionukliden in der Umwelt zur Erfüllung der Richtlinie zur Emissions- und Immissionsüberwachung bei bergbaulichen Tätigkeiten. – Report ST-IB-2, Federal Agency for Radiation Protection (BfS), Berlin.

SCHMIDT, A.P. (1998): Lead precipitates from natural gas production installations. – Journal of Geochemical Exploration, **62**, p. 193-200.

SCHMIDT, S. (2001): Untersuchungen zur Radionuklidbelastung von Oberflächenwässern, Sedimenten und Böden als Folge des Steinkohlebergbaus im Ruhr-Revier. – PhD-thesis, 189 p.; University of Essen.

SCHMIDT, S. & WIEGAND, J. (2003): Radionuclide contamination of surface waters, sediments and soil caused by coal mining activities in the Ruhr- District (Germany). – Mine Water and the Environment, **22**, p. 130-140.

SCHÖNENBERG, R. & NEUGEBAUER, J. (1997): Einführung in die Geologie Europas. – 7. Aufl., 385 S.; Rombach Verlag, Freiburg im Breisgau.

SCHÖTZIG, U. & SCHRADER, H. (2000): Halbwertszeiten und Photonen-Emissionswahrscheinlichkeiten von häufig verwendeten Radionukliden. – 5. Aufl., PTB-Bericht PTB-Ra-16/5; Physikalisch-Technische Bundesanstalt (PTB), Braunschweig.

SCHOLTEN, L.C. (1995): Approaches for regulating management of large volumes of waste containing natural radionuclides in enhanced concentrations. – KEMA nuclear report.

SCHOLTEN, L.C., ROELOFS, L.M.M., VAN DER STEEN, J. (1993): A survey of potential problems for non-nuclear industries posed by the implementation of new EC standards for natural radioactivity. – KEMA nuclear report.

SCHOTT, B. (1998): Geologische und hydrogeologische Untersuchungen zur Radionuklid-Mobilität am Mt. Vully (Canton Fribourg / CH). Diploma thesis, 124 p., University of Essen.

SCHUMANN, R.R. & GUNDERSEN, L.C.S. (1996): Geologic and climatic controls on the radon emanation coefficient. – Environmental International, **22** (1), p. S439-S446.

SCHULTE, B.F. (2005): http://www.forumfilm.de/archiv1/schwarzheide.htm.

SEELEY, F.G. & KELMERS, A.D. (1984): Geochemical information for the West Chestnut Ridge central waste disposal facility for low-level radioactive waste. – Oak Ridge National Laboratory, ORNL-6061, Oak Ridge, Tennessee, USA.

SETTLE, F. (2005): Nuclear chemistry - Uranium production. – http://www.chemcases.com/ nuclear/nc-06.htm; Washington & Lee University, USA.

SILVA, N.C., DE NADAI FERNANDES, E.A., CIPRIANI, M. & TADDEI, M.H.T. (2002): Leaching assessment of radioactive and non-radioactive elements from Brazilian phosphogypsum. – In: International Symposium on Technologically Enhanced Natural Radiation (TENR II) held in Rio de Janeiro, Brazil, 12.-17. September 1999, Proceedings published by IAEA, Vienna, Austria.

SKAUG, L.C. (1998): New designs advance spar technology into deeper water. – Oil and Gas Journal, **96**, p. 52.

SULKOWSKI, M., (2002): Speziesanalytische Untersuchungen an Boden- und Sedimentgesteinsproben auf der Grundlage von Extraktions- und Röntgenmethoden. – PhD-thesis, 231 p., University Duisburg-Essen.

SURBECK, H. (1995): Determination of natural radionuclides in drinking water; a tentative protocol. – The Science of total Environmental, **173/174**, p. 91-99.

SSK (1992): Strahlenschutzgrundsätze für die Verwahrung, Nutzung oder Freigabe von kontaminierten Materialien, Gebäuden, Flächen oder Halden aus dem Uranerzbergbau. – Veröffentlichungen der Strahlenschutzkommission, Band 23.

STEAG (1988): Strom aus Steinkohle - Stand der Kraftwerkstechnik. – 551 S.; Springer-Verlag, Berlin.

STEINHAEUSLER, F. (1988): Modifications of the natural radiation exposure and its impact on society. – Proceedings of 4th European IRPA-Congress, p. 130-142, Salzburg, Austria.

VAN DER STEEN, J., TIMMERMANS, C.W.M., VAN WEEGERS, A.W., DEGRANGE, J-P., LEFAURE, C. & SHAW, P.V. (2004): EU-project SMOPIE (contract No. FIGM-CT-2001-00176), Final report, 69p.

STP (2006): http://www.steinkohle-portal.de/content.php?id=172&lang=de. – Official homepage of the German hard coal industry (Steinkohle-Portal, STP).

STROPPE, H. (1994): Physik. – 10. Aufl., 528 S.; Fachbuchverlag Leipzig-Köln.

STRSCHV (2001): Verordnung über den Schutz vor Schäden durch ionisierende Strahlen (Strahlenschutzverordnung). – Artikel 1 der Verordnung für die Umsetzung von EURATOM-Richtlinien zum Strahlenschutz vom 26. Juli 2001. BGBl. I, Nr. 38, 1714 S., Bonn.

STULZ, P. (1973): Schlaglicht Atom. – 464 S.; Militärverlag der Deutschen Demokratischen Republik, Berlin.

TANNER, A.B. (1980): Radon migration in the ground: A supplementary review. – T. F. Gesell and W.M. Lowder, Natural radiation environment III, Vol. **1**., US Department of Energy Report CONF-780422: p. 5-56.

TESSIER, A., CAMPBELL, P.G.C., BISSON, M., (1979): Sequential extraction procedure for the speciation of particulate trace metals. – Anal. Chem., **51**, p. 844-851.

TOMZA, I. & LEBECKA, J. (1981): Radium-bearing waters in coal mines: occurrence, methods of measurements and radiation hazard. – Int. Conf. on Radiation Hazard in Mining, Golden, Co.

TREIB (2006): http://www.treibacher.com. – Official homepage of the company Treibacher Industrie AG, Treibach, Österreich.

TREIBZ (2005): www.treibacher-schleifm.com. – Official homepage of the company Treibacher Schleifmittel Zschornewitz GmbH & Co KG, Zschornewitz, Deutschland.

UIC (2006): http://www.uic.com.au/ozuran.htm. – Uranium Information Centre (UIC), official homepage of the Australian Uranium Association, Melbourne Australia.

UNSCEAR (1988): Sources and effects of Ionizing Radiation. – Report to the General Assembly by the United Nations Scientific Committee on the Effects of Atomic Radiations Sources (UNSCEAR), UN, New York.

URE, A.M., QUEVAUVILLER, PH., MUNTAU, H. & GRIEPINK, B. (1993): Speciation of heavy metals in soils and sediments - An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the Commission of the European Communities. – International Journal of Environmental Analytical Chemistry, **51**, p. 135-151.

USGS (2006): http://minerals.usgs.gov/minerals/pubs/commodity/kyanite/. – Official homepage of the U.S. Geological Survey (USGS).

VANDENHOVE, H. (2002): European sites contaminated by residues from ore-extracting and -processing industries. – International Congress Series 1225, p. 307-315.

VWU (2005): http://www.volkswagen-umwelt.de/buster/buster.asp?i=wissen_22769.asp. – Official homepage of the car manufacturer Volkswagen, Wolfsburg.

WAGNER, W. (2004): 9.2 Canadian minerals yearbook, 2004 - aluminum. – Minerals and metals sector, Natural resources Canada.

WALTER, R. (1995): Geologie von Mitteleuropa. – 6. Aufl., 566 S.; Schweizerbart'sche Verlagsbuchhandlung, Stuttgart.

WALU (2006): http://www.world-aluminium.org/production/refining/index.html. – Official homepage of the international aluminium industry.

WEISS, D. (2003): Advanced methods for re-use and disposal of TENORM. – 3rd Symposium on Radiation Protection, International Conference ENOR III, March 3. - 7. 2003; Dresden.

WHITE, G.J. & ROOD, A.S. (2001): Radon emanation from NORM-contaminated pipe scale and soil at petroleum industry sites. – Journal of Environmental Radioactivity, **54**, p. 401-413.

WHO (World Health Organization) (1959): Effects of radiation in human heredity: investigations of areas of high natural radiation. – Technical Report Series No. 166, 47 p., Geneva.

WIEGAND, J. (1999): Radon in urbanen Gebieten - Geogene und anthropogene Einflüsse auf das ^{222}Rn-Potential dargestellt am Beispiel des Ruhrgebietes. – 234 p., Habilitation thesis, University of Essen.

WIEGAND, J. & FEIGE, S. (2002): Origin of radium in high-mineralised waters. – In: Technologically enhanced natural radiation, IAEA 1271, p. 107-111.

WIESENBERGER, H. (2002): State-of-the-art for the production of fertilisers with regard to the IPPC-directive. – Monographien Band 105, 86 p., Federal Environment Agency – Austria, Wien.

WINGENDER, H.J.: (1995): Assessment of the radiological aspects of the extraction and processing of metal ores and of coal combustion in Eastern Germany. – NUKEM-report.

WOODALL, D.B., GAMBRELL, R.P., RABALAIS, N.N., DE LAUNE, R.D. (2001): Developing a method to track oil and gas produced water discharges in estuarine systems using salinity as a conservative tracer. – Marine Pollution Bulletin, **42** (11), p. 1118-1127.

ZAK, A., BIERNACKA, M., LIPINSKI, P., ISAJENKO, K. & SIBIGA, T.J. (2005): Environmental assessment of the material deposited on the former uranium mining disposal dump in Radoniow. – In: International Symposium on Naturally Occurring Radioactive Materials (NORM IV) held in Szczyrk, Poland, 17.-21. May 2004, Proceedings published by IAEA, Vienna, Austria.

ZAMPIERI, C., TROTTI, F., DESIDERI, D., JIA, G., CALDOGNETTO, E., TORRI, G., TACCONI, A., CLAUSER, G., FACCHINELLI, M., FILIPOZZI, L. & LANCIAI, M. (2005): A study concerning NORM in refractories industry. – In: International Symposium on Naturally Occurring Radioactive Materials (NORM IV) held in Szczyrk, Poland, 17.-21. May 2004, Proceedings published by IAEA, Vienna, Austria.

ZEIEN, H., BRUEMMER, G.W., (1989): Chemische Extraktionen zur Bestimmung von Schwermetallbindungsformen in Böden. – Mitt. Dtsch. Bodenkundl. Ges., **59**, p. 505-510.

Oral messages:

LACIOK, A. (2002): Oral message by Dr. Ales Laciok, Nuclear Research Institute (NRI), Rez, Czech Republic.

JOVANOVIC, P. (2002): Oral message by Dr. Peter Jovanovic, Institute of Occupational Safety (ZVD), Ljubljana, Slovenia.

Appendix

A-1 Material descriptions

The six hard rock samples from the uranium mining are geologically described in the following.

R-UO-1:

green-grey coloured slaty sandstone, shown in fig. A-1:

- glaukonitic matrix: coarse and medium grained in uniform distribution, compact
- muscovite micas: 1-2mm diameter, angular in uniform distribution, laminated, unoriented texture
- black uranium ore concentrations on slate plains: implicating the glaukonitic matrix

Fig. A-1: Raw material uranium ore R-UO-1.

R-UO-2:

red-brown coloured slaty sandstone, shown in fig. A-2:

- sandy-clayey matrix: medium and fine grained in uniform distribution, compact
- muscovite micas: 1-2mm diameter, angular in uniform distribution, laminated, unoriented texture
- black and grey uranium ore concentrations on slate plains: implicating the sandy-clayey matrix

Fig. A-2: Raw material uranium ore R-UO-2.

U-ST-1:

dark-grey and black coloured slag, shown in fig. A-3:

- matrix: massive, fine grained particles or dense structure, uniformly grained, xenomorph, uncrystallised, partly blistered, blister irregularly interspersed
- blister: maximum 5mm diameter, circular in unsymmetrical distribution, unoriented texture
- red-brown iron oxide coats on gap surfaces

Fig. A-3: Stockpile slag U-ST-1.

U-ST-2:

dark-grey slag, shown in fig. A-4:

- matrix: massive, fine grained particles or dense structure, uniformly grained, xenomorph, uncrystallised, partly blistered, blister irregularly interspersed
- blister: maximum 1mm diameter, circular in unsymmetrical distribution, unoriented texture
- red-brown iron oxide coats on gap surfaces and partly around blister
- print by machine

Fig. A-4: Stockpile slag U-ST-2.

U-ST-3:

light coloured pegmatite, shown in fig. A-5:

- matrix: massive, coarse grained quartz crystals, macrocrystallised, uniformly grained, hypidiomorph, prismatic crystals, holocrystallised, unoriented texture
- lateral uranium ore concentrations: black, medium and fine grained, hiatal, hypidiomorph and xenomorph, hemicrystallised, implicating the quartz matrix, unsymmetrical distribution, large crystals partly arranged, compact

Fig. A-5: Stockpile pegmatite dead rock U-ST-3.

U-ST-4:

red coloured brecciated sandstone, shown in fig. A-6:

- red sandstone: massive, fine grained or dense, uniformly grained, circular grains, uniformly distributed, unoriented texture
- implicating quartz veins: crystals partly green or red coloured, coarse or medium grained, macrocrystalled, hiatal structure, prismatic grains, hypidiomorph, holocrystallised, crystals perpendicularly arranged to vein structure, precipitated in tectonic gap
- uranium ore concentrations: black pitchblende spheroids, exclusively occurring on quartz crystals in the tectonic gap

Fig. A-6: Stockpile brecciated sandstone dead rock U-ST-4.

A-2 Used devices

A-2-a Gamma-spectrometer

In order to reduce influences from outside such as changing temperatures or blowing dust, the gamma-spectrometer system is installed in a dust dense laboratory of constant temperatures, it consists of three main elements (fig. A-7):

1. electronical units (shaping-amplifier, multi-channel-analyser)
2. hardware (32l-dewar with HPGe-detector and pre-amplifier on top, cylinder made of lead shielding the internal detector)
3. computer (software for data acquisition and processing)

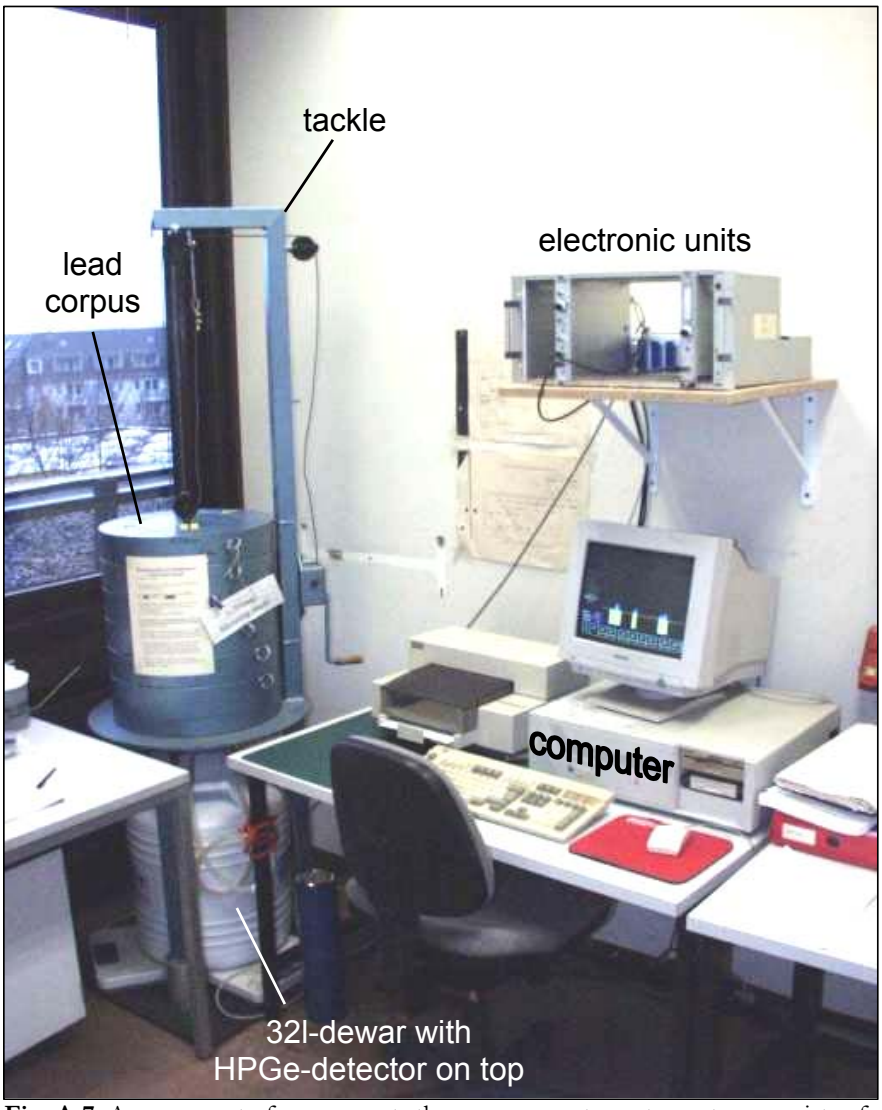

Fig. A-7: Arrangement of components the gamma-spectrometer system consists of.

Table A-1: Resolution abilities of the HPGe-detector used.

radionuclide	resolution	
^{57}Co	FWHM (**F**ull **W**idth at **H**alf **M**aximum)	1.03keV at 122keV
^{60}Co	FWHM	2.07keV at 1332keV
	FWTM (**F**ull **W**idth at **T**enth of **M**aximum)	3.94keV at 1332keV

1. Electronic units

Germanium-detectors are usually equipped with resistive feedback preamplifiers (RFP), in this case a RG-11 B/C RFP is used. The shaping-amplifier, model-number 7180, was constructed by INTERTECHNIQUE™, a subdivision of CANBERRA EURISYS™. The high voltage supply providing constantly 4kV for the detector was built by CANBERRA™ and its model-number is 3160 D. All this equipment is connected with coaxial signal and power cables.

2. Hardware

The centre of the gamma-spectrometer hardware is the high purity n-type intrinsic Germanium coaxial detector made by PRINCETON GAMMA-TECH™. The exact term is "NIGC 44" and this detector is able to evaluate low level energy peaks of 15keV minimum because of its beryllium entrance window of nearly 5cm diameter; the maximum is reached at the highest energies of 2000keV. The distance detector-window amounts 5mm. The Germanium crystal, being permanently cooled by nitrogen stored in a 32l-standard-dewar, is formed as a nearly coaxial shape with 65mm length and 50.4mm diameter, always being kept under constant high-voltage of 4kV. Its ability of respond towards ^{60}Co as the relative efficiency is noticed with 43.8% of a NaI-crystal, measured at 25cm source-detector-distance relative to a 3"•3" NaI-crystal. The peak to Compton ratio is indicated with 58:1 at 1332keV, the resolution abilities at low and high energies are given in table A-1. The Germanium crystal is covered by a cylinder made of aged lead in a size of approximate 0.5m height and 0.45m diameter. The samples can be put from above into the vessel respective on the detector when the lid is opened by a tackle (fig. A-7). The system is calibrated for ^{226}Ra detection limits of 1Bq/kg for solids and 0.5Bq/l for liquids, those of ^{234}Th, ^{210}Pb, ^{228}Ac are slightly higher, of ^{208}Tl slightly lower.

3. Software

For the data acquisition and processing the software "InterWinner 5.0" made by ORTEC™ is installed. The radionuclide's activity is calculated as follows:

$$activity = \frac{counts_{netto} \cdot coefficient_{nuclide}}{lifetime}$$

$$counts_{netto} = counts_{gross} - background$$

$$coefficient_{nuclide} = \frac{1}{efficiency \cdot branching\,ratio_{nuclide}}$$

$counts_{gross}$: sum of the counts within the ROI ("Region Of Interest"), excluding the first and last 3 channels of the ROI

The background is given by:

$$background = \frac{averagecounts_{first\ 3\ channels} + averagecounts_{last\ 3\ channels}}{2} \cdot width_{ROI}$$

$$width_{ROI} = channel_{end} - channel_{start} + 1 - 6$$

A-2-b Calibration liquid

The used 250ml calibration liquid provided by Dr. Thomas Bünger from the German Federal Agency for Radiation Protection (BfS), Berlin, contains the following artificial radionuclides by activity:

Table A-2: Activity concentrations of the artificial radionuclides contained in the BfS-calibration liquid.

radionuclide	**emitted γ-line [keV]**	**amount of accurate measurements**	**activity [Bq]**	**error range [Bq]**
^{241}Am	59	separate calibration liquid	43.25	-/-
^{57}Co	122, 137	280	2.98	0.2
^{134}Cs	605, 796	281	11.85	0.8
^{137}Cs	661	281	53.5	1.4
^{54}Mn	835	288	2.28	0.1
^{60}Co	1173, 1332	288	51.25	1.3

A-2-c Correction of ^{234}Th and ^{210}Pb for self-absorption

The point source is put centrically on top of the cylindrical box the sample material is stored (grey coloured), which is put on three empty cylindrical boxes for extending the distance material-detector (fig. A-8). This arrangement is found to be most appropriate by empirical measurements. The measured counts are related to those acquired from the point source without any self-absorption (empty sample box) and result in coefficients, which are calculated for both energies 45.7keV and 59.5keV. These coefficients are the factors the obtained activity concentraions of ^{210}Pb and ^{234}Th must be multiplied with. All the solid TENORM samples' self-absorption coefficients are presented in table A-3.

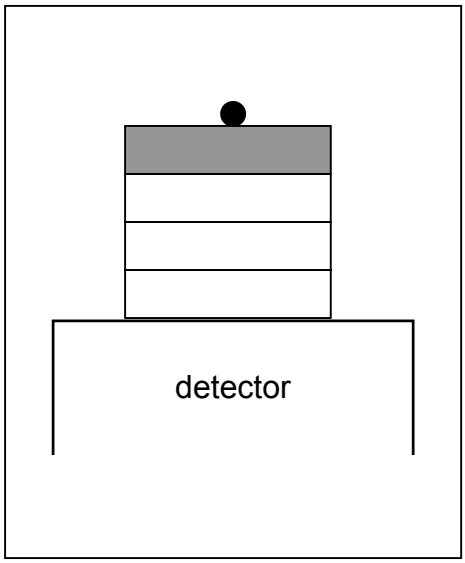

Fig. A-8: Arrangement of point source and cylindrical boxes on the detector.

Table A-3: ^{210}Pb and ^{234}Th self-absorption coefficients (SAC) for the solid TENORM samples.

sample		45.7keV		59.5keV	
		counts	**SAC (^{210}Pb)**	counts	**SAC (^{234}Th)**
NP363-standard		3455	**1**	9634	**1**
phosphate industry	R-PO-1	1657	**1.41**	6749	**1.19**
	R-PO-2	673	**2.03**	4372	**1.45**
	W-PG-1	1932	**1.32**	7699	**1.12**
	P-F-1	2321	**1.21**	8123	**1.09**
	P-F-2	2122	**1.26**	7733	**1.11**
aluminium industry	R-AO-1	1915	**1.32**	6939	**117**
	R-AO-2	2250	**1.23**	7681	**1.12**
	W-RS-1	1462	**1.49**	7037	**1.17**
refractory industry	R-ZS-1	21	**5.13**	361	**3.41**
	W-FD-1	3945	**0.94**	11458	**0.92**
	P-FZM-1	73	**3.94**	1400	**2.26**
	P-FZM-2	177	**3.13**	2808	**1.74**
crude oil exploitation	W-SL-1	599	**2.12**	4058	**1.49**
	W-SL-2	377	**2.49**	4649	**1.41**
	W-SC-1	844	**1.87**	4323	**1.57**
	W-SC-2	245	**2.85**	2653	**1.78**
hard coal extraction	U-S-1	2811	**1.11**	9236	**1.02**
	U-S-2	2797	**1.11**	8956	**1.04**
	U-S-3	2482	**1.17**	7572	**1.13**
	U-S-4	2239	**1.23**	6956	**1.17**
thorium compounds industry	U-SO-1	224	**2.93**	3254	**1.64**
	U-SO-2	2098	**1.27**	7756	**1.11**
	U-SO-3	1918	**1.32**	7656	**1.12**
	U-SO-4	2774	**1.11**	8540	**1.06**
uranium industry	R-UO-1	2823	**1.10**	8069	**1.09**
	R-UO-2	3244	**1.03**	6675	**1.19**
	U-ST-1	214	**2.97**	2551	**1.81**
	U-ST-2	583	**2.14**	2542	**1.81**
	U-ST-3	1469	**1.49**	6216	**1.24**
	U-ST-4	724	**1.98**	6247	**1.23**
	U-S-5	2469	**1.18**	8433	**1.07**
	U-S-6	2783	**1.11**	9041	**1.03**

Used point sorce: NP363, made by ISOTRAK™ (now part of QSA GLOBAL™ INC.)
radionuclides stored in ionexchange pellets
diameter: 25mm
height: 3mm
active zone: 3mm
total activity: almost 20kBq, ± 3%
reference date: 01. August 2005, 12.00h

contained radionuclides: ^{241}Am: 9.64kBq
γ-line emitted at **59.54keV**, yield per decay: 35.9%, $T_{1/2}$: 432.2a
^{152}Eu: 9.89kBq
γ-line emitted at **45.7keV**, yield per decay: 14.9% $T_{1/2}$: 13.54a

[SCHÖTZIG & SCHRADER, 2000]

A-2-d Radon measuring devices

Scintillation counter LUK 4E made by RADON V.O.S.™:

- consists of the measuring unit LUK 4A and an external sample changer
- two volume types of glass LUCAS cells (125ml and 600ml) are useable

Typical background values: 125ml-LUCAS cells: 1 to 2 counts, measuring time: 100s
600ml-LUCAS cells: 20 to 40 counts, measuring time: 1000s

Detection efficiencies: 125ml-LUCAS cells: 0.78 [78%]
600ml-LUCAS cells: 0.7 [70%]

RAD7 made by NITON™:

- consists of a 700ml-cell lined with an electric conductor, the alpha-detector is positioned in the centre of the cell
- measuring spectrum covers energy range 0-10MeV, devided into 200 individual measurement channels, each channel has 0.05 MeV
- radon concentration calculated as follows: $c_{Rn} = \frac{c_m}{factor_{equipment}}$

c_{Rn}: ^{222}Rn-concentration [Bq/m^3]
c_m: counts measured

$factor_{equipment}$: sensitivity 0.0114 $\frac{cpm}{Bq/m^3}$ {cpm: counts per minute}

uncertainty: ± 5%
detection limit: 2.5Bq/m^3

A-2-e Gamma dose rate measuring device

- portable scintillation counter "M3 16-3 Gate Frisker" made by LUDLUM™, Texas/USA
- equipped with 2"•2" NaI-crystal
- 10 kcpm (kilo counts per minute) correspond to 100 nSv/h

A-3 Radionuclide portions extracted by BCR procedure

Table A-4: Extracted portions from the phosphate samples R-PO-1, R-PO-2 and W-PG-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
R-PO-1, <2mm	^{238}U	1484 ± 100	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1484	100
	^{226}Ra	1479 ± 98	14 ± 2.2	388 ± 61	26	5.7 ± 1	176 ± 31	12	20 ± 1.2	762 ± 44	52	153	10
	^{214}Pb	1556 ± 107	13 ± 2.2	361 ± 61	23	6.3 ± 1	196 ± 31	13	20 ± 1.1	770 ± 42	50	230	15
	^{214}Bi	1402 ± 88	15 ± 2.2	416 ± 61	30	5 ± 1	155 ± 31	11	20 ± 1.2	754 ± 46	54	76	5
	^{210}Pb	1603 ± 91	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1603	100
	^{228}Ra	18 ± 4.8	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	18	100
	^{228}Th	15 ± 3.3	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	15	100
R-PO-2, <2mm	^{238}U	19 ± 7.8	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	19	100
	^{226}Ra	31 ± 2.4	2.7 ± 0.7	94 ± 24	30	3.8 ± 0.7	134 ± 25	12	2.7 ± 0.6	114 ± 26	57	0	0
	^{214}Pb	32 ± 2.5	2.7 ± 0.7	94 ± 24	28	3.8 ± 0.7	134 ± 25	13	3.3 ± 0.6	143 ± 26	58	0	0
	^{214}Bi	29 ± 2.3	2.7 ± 07	94 ± 24	31	3.8 ± 0.7	134 ± 25	9	2 ± 0.6	86 ± 26	57	0	0
	^{210}Pb	15 ± 7.1	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	15	100
	^{228}Ra	80 ± 6.4	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	80	100
	^{228}Th	86 ± 6	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	86	100
W-PG-1, <2mm	^{238}U	40 ± 13.3	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	40	100
	^{226}Ra	41 ± 3.5	6.3 ± 1	223 ± 34	48	2.5 ± 0.7	94 ± 26	20	3.5 ± 0.6	145 ± 25	31	0	0
	^{214}Pb	43 ± 3.5	6.1 ± 0.9	216 ± 32	48	2.3 ± 0.6	86 ± 23	20	3.5 ± 0.6	147 ± 25	32	0	0
	^{214}Bi	39 ± 3.5	6.5 ± 1	230 ± 35	48	2.7 ± 0.8	101 ± 30	21	3.4 ± 0.6	143 ± 25	30	0	0
	^{210}Pb	41 ± 13.3	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	41	100
	^{228}Ra	60 ± 7	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	60	100
	^{228}Th	50 ± 5.1	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	50	100

n.d.: not detected

Table A-5: Extracted portions from the phosphate samples P-F-1 and P-F-2 and the aluminium sample R-AO-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
P-F-1, <2mm	^{238}U	842 ± 56	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	842	100
	^{226}Ra	149 ± 11	1.6 ± 0.6	50 ± 17	4	20 ± 1.3	629 ± 40	52	2.1 ± 0.8	76 ± 28	44	0	0
	^{214}Pb	160 ± 12	1.4 ± 0.5	44 ± 16	4	20 ± 1.2	629 ± 39	45	1.8 ± 0.7	67 ± 26	51	0	0
	^{214}Bi	137 ± 10	1.8 ± 0.6	56 ± 19	5	20 ± 1.3	629 ± 42	56	2.3 ± 0.8	85 ± 30	38	0	0
	^{210}Pb	164 ± 27	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	164	100
	^{228}Ra	14 ± 6.8	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	14	100
	^{228}Th	6.9 ± 1.1	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	6.9	100
P-F-2, <2mm	^{238}U	846 ± 54	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	846	100
	^{226}Ra	275 ± 19	8.5 ± 1.2	233 ± 32	51	4.6 ± 0.8	130 ± 22	28	2.9 ± 0.6	98 ± 19	21	0	0
	^{214}Pb	290 ± 20	8.3 ± 1.1	227 ± 30	52	4.3 ± 0.8	123 ± 23	28	2.8 ± 0.5	95 ± 17	21	0	0
	^{214}Bi	259 ± 17	8.7 ± 1.2	239 ± 33	50	4.8 ± 0.7	137 ± 20	28	3 ± 0.6	101 ± 20	21	0	0
	^{210}Pb	268 ± 25	n.d.	-/-	-/-	19 ± 6.8	544 ± 195	84	3.1 ± 1	105 ± 33	17	0	0
	^{228}Ra	<11	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	<11	100
	^{228}Th	<6.9	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	<6.9	100
R-AO-1, <2mm	^{238}U	130 ± 19	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	130	100
	^{226}Ra	231 ± 17	25 ± 1.5	982 ± 58	78	4 ± 0.7	150 ± 24	11	3 ± 0.9	129 ± 38	10	0	0
	^{214}Pb	216 ± 15	26 ± 1.5	988 ± 58	81	3.6 ± 0.7	134 ± 26	11	2.2 ± 0.8	99 ± 36	8	0	0
	^{214}Bi	245 ± 19	26 ± 1.5	976 ± 58	75	4.5 ± 0.7	167 ± 22	12	3.5 ± 0.9	158 ± 41	12	0	0
	^{210}Pb	422 ± 38	5.3 ± 0.5	205 ± 20	49	n.d.	-/-	-/-	n.d.	-/-	-/-	217	51
	^{228}Ra	176 ± 16	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	176	100
	^{228}Th	156 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	156	100

n.d.: not detected

Table A-6: Extracted portions from the aluminium samples R-AO-2 and W-RS-1 and the refractory sample R-ZS-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR			3. BCR			
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
R-AO-2, <2mm	^{238}U	862 ± 72	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	862	100
	^{226}Ra	2182 ± 159	34 ± 1.3	1301 ± 51	56	13 ± 1.2	486 ± 47	20	13 ± 1	572 ± 44	24	0	0
	^{214}Pb	2000 ± 137	34 ± 1.3	1321 ± 51	56	13 ± 1.2	505 ± 47	20	13 ± 0.9	560 ± 40	24	0	0
	^{214}Bi	2363 ± 180	33 ± 1.3	1282 ± 51	56	12 ± 1.2	466 ± 47	20	13 ± 1.1	586 ± 49	24	0	0
	^{210}Pb	3927 ± 293	17 ± 8	661 ± 310	17	9.3 ± 6.9	361 ± 268	9	n.d.	-/-	-/-	2492	64
	^{228}Ra	169 ± 17	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	169	100
	^{228}Th	147 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	147	100
W-RS-1, <2mm	^{238}U	191 ± 26	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	191	100
	^{226}Ra	195 ± 15	5 ± 0.8	201 ± 30	42	3.4 ± 0.7	133 ± 28	28	3.2 ± 0.8	145 ± 37	30	0	0
	^{214}Pb	186 ± 13	5.2 ± 0.8	194 ± 30	45	2.8 ± 0.7	110 ± 28	25	2.8 ± 0.7	129 ± 32	30	0	0
	^{214}Bi	203 ± 16	5.6 ± 0.8	208 ± 30	40	4 ± 0.7	157 ± 28	30	3.5 ± 0.9	161 ± 41	30	0	0
	^{210}Pb	329 ± 39	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	329	100
	^{228}Ra	516 ± 43	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	516	100
	^{228}Th	459 ± 36	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	459	100
R-ZS-1, <2mm	^{238}U	2575 ± 222	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	2575	100
	^{226}Ra	2930 ± 215	5 ± 1	160 ± 34	5	2 ± 0.7	81 ± 23	3	1.3 ± 0.9	53 ± 36	2	2636	90
	^{214}Pb	2610 ± 179	4.3 ± 0.9	153 ± 32	6	2.2 ± 0.7	79 ± 25	3	1.5 ± 0.8	63 ± 34	2	2315	89
	^{214}Bi	3249 ± 250	4.7 ± 1	167 ± 36	5	2.3 ± 0.6	83 ± 22	3	1 ± 0.9	42 ± 38	1	2957	91
	^{210}Pb	2610 ± 288	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	2610	100
	^{228}Ra	762 ± 61	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	762	100
	^{228}Th	690 ± 53	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	690	100

n.d.: not detected

Table A-7: Extracted portions from the refractory samples W-FD-1, P-FZM-1 and P-FZM-2; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR			3. BCR			
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
W-FD-1, <0.1mm	^{238}U	289 ± 68	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	289	100
	^{226}Ra	295 ± 23	5 ± 1	180 ± 35	29	5.2 ± 0.9	200 ± 35	33	5.3 ± 0.9	232 ± 40	38	0	0
	^{214}Pb	283 ± 21	4.5 ± 0.9	163 ± 33	28	4.5 ± 0.9	173 ± 35	29	5.5 ± 1	243 ± 44	42	0	0
	^{214}Bi	306 ± 26	5.4 ± 1	196 ± 36	30	5.9 ± 0.9	227 ± 35	36	5 ± 0.8	221 ± 35	34	0	0
	^{210}Pb	162,400 ± 14,260	8.7 ± 6.6	317 ± 240	0.2	456 ± 6.7	17,569 ± 258	11	1000 ± 78	44,201 ± 3456	27	100,313	62
	^{228}Ra	74 ± 18	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	74	100
	^{228}Th	80 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	80	100
P-FZM-1, <2mm	^{238}U	1829 ± 129	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1829	100
	^{226}Ra	1601 ± 106	7 ± 1	232 ± 33	15	2 ± 0.7	53 ± 21	3	9.1 ± 0.7	347 ± 25	22	969	60
	^{214}Pb	1680 ± 116	6.6 ± 1	216 ± 33	13	1.3 ± 0.6	42 ± 19	3	9.3 ± 0.6	355 ± 23	21	1068	64
	^{214}Bi	1522 ± 96	7.6 ± 1	248 ± 33	16	2 ± 0.7	64 ± 23	4	8.9 ± 0.7	340 ± 27	22	870	57
	^{210}Pb	932 ± 92	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	932	100
	^{228}Ra	388 ± 26	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	388	100
	^{228}Th	369 ± 25	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	369	100
P-FZM-2, <0.1mm	^{238}U	3913 ± 260	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	3913	100
	^{226}Ra	4206 ± 278	3.5 ± 0.9	109 ± 25	3	9.5 ± 1.2	301 ± 37	7	1.5 ± 0.6	58 ± 23	1	3738	89
	^{214}Pb	4421 ± 306	3.4 ± 0.8	108 ± 24	2	10 ± 1.2	318 ± 38	7	1.2 ± 0.6	46 ± 23	1	3949	89
	^{214}Bi	3990 ± 249	3.5 ± 0.9	111 ± 26	3	8.9 ± 1.1	283 ± 35	7	1.8 ± 0.6	69 ± 23	2	3527	88
	^{210}Pb	950 ± 124	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	950	100
	^{228}Ra	853 ± 55	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	853	100
	^{228}Th	780 ± 52	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	780	100

n.d.: not detected

Table A-8: Extracted portions from the oil exploitation samples W-SL-1, W-SL-2 and W-SC-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR			3. BCR			
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
W-SL-1, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	17,570 ± 1287	1.5 ± 0.4	55 ± 15	0.3	2.2 ± 0.5	84 ± 20	0.5	7.8 ± 0.6	377 ± 27	2	17,054	97
	^{214}Pb	16,010 ± 1092	2.1 ± 0.3	77 ± 11	0.5	2.5 ± 0.4	98 ± 16	0.6	8.3 ± 0.5	401 ± 24	3	15,434	96
	^{214}Bi	19,130 ± 1481	0.9 ± 0.5	33 ± 18	0.2	1.8 ± 0.6	70 ± 23	0.4	7.3 ± 0.6	353 ± 29	2	18,674	98
	^{210}Pb	27,048 ± 2405	128 ± 13	4693 ± 466	17	46 ±6 .3	1795 ± 246	7	89 ± 9.4	4298 ± 454	16	16,261	60
	^{228}Ra	3832 ± 303	1.3 ± 0.9	48 ± 33	1	n.d.	-/-	-/-	2 ± 0.9	97 ± 44	3	3618	96
	^{228}Th	4185 ± 315	2.1 ± 0.6	77 ± 22	2	2.7 ± 0.6	105 ± 23	3	2.7 ± 0.6	130 ± 29	3	3872	93
W-SL-2, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	48,100 ± 3526	3.9 ± 0.6	129 ± 20	0.3	5.4 ± 0.6	173 ± 19	0.4	10 ± 0.6	438 ± 25	0.9	47,360	98
	^{214}Pb	44,120 ± 3007	3.8 ± 0.5	126 ± 17	0.3	5.8 ± 0.5	187 ± 16	0.4	11 ± 0.6	471 ± 25	1	43,337	98
	^{214}Bi	52,080 ± 4045	4 ± 0.7	132 ± 23	0.3	5 ± 0.7	161 ± 23	0.3	9.6 ± 0.6	404 ± 25	0.8	51,383	99
	^{210}Pb	46,125 ± 4108	32 ± 5.3	1043 ± 175	2	12 ± 4.6	380 ± 148	0.8	174 ± 17	7321 ± 719	16	37,381	81
	^{228}Ra	12,840 ± 1006	1.8 ± 1.1	60 ± 36	0.5	2.1 ± 1.2	68 ± 39	0.5	3.7 ± 1	156 ± 42	1	12,557	98
	^{228}Th	13,020 ± 978	1.8 ± 0.9	60 ± 30	0.5	2.4 ± 0.9	77 ± 29	0.6	4.2 ± 0.9	177 ± 38	1	12,703	98
W-SC-1, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	3705 ± 270	0.7 ± 0.4	16 ± 10	0.4	0.9 ± 0.5	22 ± 12	0.6	9.3 ± 0.6	299 ± 18	8	3368	91
	^{214}Pb	3378 ± 231	0.5 ± 0.3	13 ± 8	0.4	0.9 ± 0.4	23 ± 10	0.7	10 ± 0.5	321 ± 16	9	3021	89
	^{214}Bi	4032 ± 309	0.8 ± 0.5	20 ± 13	0.5	0.8 ± 0.5	21 ± 13	0.5	8.6 ± 0.6	276 ± 19	7	3715	92
	^{210}Pb	44,821 ± 3954	619 ± 58	15,489 ± 1459	67	68 ± 8.5	1766 ± 219	7	184 ± 18	5913 ± 578	26	0	0
	^{228}Ra	1162 ± 93	1.9 ± 0.8	48 ± 20	4	n.d.	-/-	-/-	2.1 ± 0.9	68 ± 29	6	997	90
	^{228}Th	1335 ± 101	2.1 ± 0.9	53 ± 23	4	1.2 ± 0.9	31 ± 23	2	2.4 ± 0.6	77 ± 19	6	1174	88

n.d.: not detected

Table A-9: Extracted portions from the oil exploitation sample W-SC-2 and the hard coal mining samples U-S-1 and U-S-2; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
W-SC-2, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	9235 ± 677	1.7 ± 0.5	51 ± 15	0.6	6 ± 0.6	191 ± 18	2	15 ± 0.8	602 ± 30	7	8390	91
	^{214}Pb	8279 ± 565	2.2 ± 0.4	67 ± 12	0.8	6.6 ± 0.5	210 ± 16	3	16 ± 0.7	647 ± 28	8	7355	89
	^{214}Bi	10,190 ± 788	1.2 ± 0.6	36 ± 18	0.4	5.4 ± 0.6	171 ± 19	2	14 ± 0.8	557 ± 32	6	9425	93
	^{210}Pb	45,559 ± 4011	194 ± 2	5861 ± 60	13	56 ± 7.1	1783 ± 226	4	163 ± 16	6433 ± 643	14	31,483	69
	^{228}Ra	1427 ± 114	n.d.	-/-	-/-	n.d.	-/-	-/-	2.3 ± 1	91 ± 40	6	1212	94
	^{228}Th	1794 ± 135	2.4 ± 0.9	73 ± 27	4	2.1 ± 0.9	64 ± 29	4	3 ± 0.6	118 ± 24	7	1536	86
U-S-1, <2mm	^{238}U	19 ± 1.1	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	19	100
	^{226}Ra	41 ± 2.7	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	41	100
	^{214}Pb	40 ± 2.7	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	40	100
	^{214}Bi	41 ± 2.6	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	41	100
	^{210}Pb	55 ± 12	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	55	100
	^{228}Ra	28 ± 2.3	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	28	100
	^{228}Th	26 ± 2.1	2.1 ± 0.9	78 ± 34	24	2.2 ± 0.9	80 ± 34	40	1.5 ± 0.6	72 ± 29	46	0	0
U-S-2, <2mm	^{238}U	138 ± 27	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	138	100
	^{226}Ra	541 ± 32	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	541	100
	^{214}Pb	525 ± 33	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	525	100
	^{214}Bi	556 ± 31	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	556	100
	^{210}Pb	330 ± 38	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	330	100
	^{228}Ra	63 ± 4.8	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	63	100
	^{228}Th	67 ± 4.5	1.5 ± 0.6	56 ± 23	24	2.5 ± 0.9	93 ± 35	39	1.8 ± 0.6	85 ± 28	37	0	0

n.d.: not detected

Table A-10: Extracted portions from the hard coal mining samples U-S-3 and U-S-4 and the thorium sample U-SO-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR			3. BCR			
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
U-S-3, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	1314 ± 78	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1314	100
	^{214}Pb	1276 ± 81	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1276	100
	^{214}Bi	1352 ± 76	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1352	100
	^{210}Pb	650 ± 68	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	650	100
	^{228}Ra	142 ± 9.8	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	142	100
	^{228}Th	178 ± 11	1.8 ± 0.9	69 ± 34	47	1.6 ± 0.9	58 ± 35	31	1.1 ± 0.6	58 ± 29	32	0	0
U-S-4, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	1248 ± 75	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1248	100
	^{214}Pb	1207 ± 77	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1207	100
	^{214}Bi	1288 ± 72	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	1288	100
	^{210}Pb	523 ± 61	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	523	100
	^{228}Ra	181 ± 12	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	181	100
	^{228}Th	199 ± 12	2.2 ± 0.9	79 ± 34	29	2.4 ± 0.9	95 ± 36	34	2.3 ± 0.6	100 ± 29	37	0	0
U-SO-1, <2mm	^{238}U	16,112 ± 3102	n.d.	-/-	-/-	22 ± 7.5	798 ± 274	8	n.d.	-/-	-/-	9273	92
	^{226}Ra	1024 ± 249	n.d.	-/-	-/-	1.5 ± 0.8	53 ± 29	6	n.d.	-/-	-/-	971	94
	^{214}Pb	733 ± 204	n.d.	-/-	-/-	1.4 ± 0.7	52 ± 26	7	n.d.	-/-	-/-	682	93
	^{214}Bi	1314 ± 293	n.d.	-/-	-/-	1.5 ± 0.9	55 ± 33	4	n.d.	-/-	-/-	1259	96
	^{210}Pb	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{228}Ra	501,400 ± 39,160	182 ± 6.2	6557 ± 223	1	489 ± 14	17,889 ± 527	4	866 ± 37	39,078 ± 1665	8	437,876	87
	^{228}Th	417,000 ± 31,350	94 ± 3.6	3394 ± 130	0.8	247 ± 8.4	9032 ± 307	2	708 ± 40	31,949 ± 1800	8	372,625	89

n.d.: not detected

Table A-11: Extracted portions from the thorium samples U-SO-2, U-SO-3 and U-SO-4; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
U-SO-2, <2mm	^{238}U	2398 ± 206	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	2398	100
	^{226}Ra	1197 ± 88	8.4 ± 0.9	287 ± 29	17	22 ± 1.1	801 ± 39	47	15 ± 1.1	637 ± 46	37	0	0
	^{214}Pb	1100 ± 76	7.9 ± 0.8	270 ± 27	17	23 ± 1	839 ± 37	50	13 ± 1.1	548 ± 48	33	0	0
	^{214}Bi	1293 ± 99	8.9 ± 0.9	304 ± 31	18	21 ±1.1	762 ± 41	41	17 ± 1	726 ± 44	40	0	0
	^{210}Pb	1963 ± 215	5 ± 0.5	171 ± 17	9	7.5 ± 2.3	276 ± 85	14	n.d.	-/-	-/-	1516	77
	^{228}Ra	10,960 ± 857	61 ± 2.3	2073 ± 79	19	70 ± 2.3	2562 ± 85	23	57 ± 2.4	2479 ± 104	23	3847	35
	^{228}Th	9279 ± 699	32 ± 2.1	1077 ± 72	12	32 ± 1.8	1192 ± 66	13	56 ± 2.7	2427 ± 117	26	4582	49
U-SO-3, <2mm	^{238}U	1762 ± 163	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	880 ± 65	4.8 ± 0.9	151 ± 28	9	34 ± 2	1068 ± 61	65	11 ± 1.1	433 ± 42	27	0	0
	^{214}Pb	814 ± 57	4.6 ± 0.8	144 ± 25	8	36 ± 1.9	1117 ± 59	66	11 ± 1	449 ± 40	27	0	0
	^{214}Bi	945 ± 73	5 ± 1	157 ± 31	10	33 ± 2	1017 ± 62	64	11 ± 1.1	417 ± 44	27	0	0
	^{210}Pb	1596 ± 179	n.d.	-/-	-/-	n.d.	-/-	-/-	9.5 ± 6.1	378 ± 242	24	462	76
	^{228}Ra	8915 ± 697	51 ± 2.3	1601 ± 72	18	96 ± 3.8	3006 ± 119	34	44 ± 2.3	1757 ± 92	20	2552	29
	^{228}Th	7599 ± 573	25 ± 1.8	772 ± 57	11	45 ± 3	1395 ± 94	18	47 ± 2.7	1848 ± 107	24	3583	47
U-SO-4, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	18 ± 2.1	5.1 ± 1	189 ± 36	70	1.1 ± 0.9	39 ± 32	14	1 ± 0.7	44 ± 31	16	0	0
	^{214}Pb	16 ± 1.6	4.8 ± 0.9	180 ± 34	71	1 ± 1	37 ± 37	14	0.8 ± 0.8	35 ± 35	14	0	0
	^{214}Bi	20 ± 2.5	5.3 ± 1	198 ± 37	68	1.1 ± 0.7	41 ± 26	14	1.2 ± 0.6	53 ± 26	18	0	0
	^{210}Pb	38 ± 7.9	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{228}Th	37 ± 4.5	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-

n.d.: not detected

Table A-12: Extracted portions from the uranium samples R-UO-1, R-UO-2 and W-T-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
R-UO-1, <0.1mm	^{238}U	130,900 ± 15,290	853 ± 295	32,201 ± 11,137	27	187 ± 27	7268 ± 1032	6	346 ± 120	16,940 ± 5872	14	62,593	53
	^{226}Ra	94,215 ± 5501	244 ± 7.7	9192 ± 289	10	514 ± 16	20,030 ± 606	21	300 ± 9.2	14,659 ± 448	16	50,334	53
	^{214}Pb	92,400 ± 4676	266 ± 7.9	10,041 ± 298	11	557 ± 16	21,699 ± 627	24	322 ± 9.4	15,738 ± 460	17	44,921	49
	^{214}Bi	96,030 ± 6325	221 ± 7.4	8343 ± 279	9	471 ± 15	18,361 ± 584	19	278 ± 8.9	13,580 ± 436	14	55,747	58
	^{210}Pb	123,420 ± 8602	312 ± 32	11,778 ± 1201	11	320 ± 33	12,452 ± 1278	11	255 ± 28	12,479 ± 1365	11	75,491	67
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{228}Th	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
R-UO-2, <0.1mm	^{238}U	832,580 ± 151,800	4931 ± 1702	187,353 ± 64667	36	4336 ± 1496	167,333 ± 57,733	32	3392 ± 1171	161,942 ± 55,906	32	0	0
	^{226}Ra	894,650 ± 52,145	58 ± 2.5	2193 ± 95	0.2	182 ± 6.5	7039 ± 249	0.8	138 ± 4.9	6588 ± 234	0.7	878,829	98
	^{214}Pb	884,400 ± 44800	65 ± 2.9	2486 ± 110	0.3	202 ± 7.3	7784 ± 282	0.9	152 ± 5.5	7252 ± 263	0.8	866,878	98
	^{214}Bi	904,900 ± 59,490	50 ± 2.1	1901 ± 80	0.2	163 ± 5.6	6294 ± 216	0.7	124 ± 4.3	5924 ± 205	0.7	890,780	98
	^{210}Pb	856,000 ± 61,024	1072 ± 103	40,730 ± 3914	8	5933 ± 557	228,964 ± 21,496	43	3573 ± 336	170,583 ± 16,041	32	94,722	18
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{228}Th	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
W-T-1, <2mm	^{238}U	1553 ± 246	12 ± 5.2	466 ± 203	30	n.d.	-/-	-/-	n.d.	-/-	-/-	1087	70
	^{226}Ra	4691 ± 280	27 ± 1.2	1034 ± 45	22	0.9 ± 0.9	35 ± 34	0.7	7 ± 0.6	346 ± 27	7	3277	70
	^{214}Pb	4571 ± 289	28 ± 1.1	1110 ± 43	24	0.9 ± 0.8	35 ± 31	0.8	7.7 ± 0.5	376 ± 25	8	3051	67
	^{214}Bi	4810 ± 271	25 ± 1.2	957 ± 47	20	0.9 ± 0.9	34 ± 35	0.7	6.4 ± 0.6	316 ± 29	7	3503	73
	^{210}Pb	9189 ± 748	27 ± 5.8	1057 ± 227	12	8.4 ± 4.4	331 ± 173	3.6	n.d.	-/-	-/-	7801	85
	^{228}Ra	31 ± 3.3	2.4 ± 1.2	93 ± 47	100	n.d.	-/-	-/-	n.d.	-/-	-/-	0	0
	^{228}Th	32 ± 2.7	1.4 ± 0.9	54 ± 35	27	2 ± 0.9	77 ± 35	36	1.5 ± 0.6	75 ± 29	36	0	0

n.d.: not detected

Table A-13: Extracted portions from the uranium samples W-T-2, W-T-3 and W-T-4; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
W-T-2, <2mm	^{238}U	1875 ± 297	14 ± 5.2	537 ± 200	29	7.2 ± 2.3	281 ± 90	15	n.d.	-/-	-/-	1057	56
	^{226}Ra	5556 ± 332	44 ± 1.6	1669 ± 60	30	21 ± 1	819 ± 37	15	8.3 ± 0.6	406 ± 27	7	2662	48
	^{214}Pb	5433 ± 344	46 ± 1.5	1765 ± 58	33	23 ± 0.9	897 ± 35	16	8.8 ± 0.5	433 ± 25	8	2338	43
	^{214}Bi	5678 ± 320	41 ± 1.6	1573 ± 61	28	19 ± 1	740 ± 39	13	7.7 ± 0.6	379 ± 30	7	2985	53
	^{210}Pb	10,260 ± 833	46 ± 7.1	1765 ± 272	17	9.5 ± 4.7	370 ± 183	4	n.d.	-/-	-/-	8124	79
	^{228}Ra	29 ± 3.2	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	29	100
	^{228}Th	27 ± 2.4	2.7 ± 0.9	104 ± 35	37	2.7 ± 0.9	105 ± 35	37	1.5 ± 0.6	74 ± 30	26	0	0
W-T-3, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	9754 ± 583	5 ± 0.6	194 ± 23	2	127 ± 4	4912 ± 144	50	13 ± 0.7	615 ± 34	6	4034	41
	^{214}Pb	9601 ± 607	5.3 ± 0.5	206 ± 19	2	138 ± 3.8	5358 ± 148	56	14 ± 0.7	666 ± 34	7	3371	35
	^{214}Bi	9907 ± 558	4.7 ± 0.7	181 ± 27	2	115 ± 3.6	4465 ± 140	45	12 ± 0.7	564 ± 34	6	4696	47
	^{210}Pb	15,910 ± 1291	59 ± 8.5	2269 ± 328	14	37 ± 7.9	1437 ± 307	9	8 ± 3.9	389 ± 190	2	11,815	74
	^{228}Ra	33 ± 4	1.7 ± 1.2	65 ± 46	100	n.d.	-/-	-/-	n.d.	-/-	-/-	0	0
	^{228}Th	31 ± 3	1.3 ± 0.6	49 ± 23	25	2.4 ± 0.9	93 ± 35	46	1.2 ± 0.6	58 ± 29	29	0	0
W-T-4, <2mm	^{238}U	1773 ± 280	n.d.	-/-	-/-	6.4 ± 2.2	248 ± 85	14	n.d.	-/-	-/-	1525	86
	^{226}Ra	3011 ± 180	11 ± 0.7	439 ± 27	15	9 ± 0.7	363 ± 25	12	4 ± 0.5	199 ± 22	7	2010	67
	^{214}Pb	2955 ± 187	12 ± 0.6	474 ± 23	16	10 ± 0.6	388 ± 23	13	4.6 ± 0.4	223 ± 19	8	1871	63
	^{214}Bi	3066 ± 173	10 ± 0.8	403 ± 31	13	8.7 ± 0.7	338 ± 27	11	3.6 ± 0.5	274 ± 24	6	2150	70
	^{210}Pb	7844 ± 639	28 ± 5.3	1068 ± 206	14	10 ± 4.4	396 ± 171	5	n.d.	-/-	-/-	6381	81
	^{228}Ra	28 ± 2.5	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	28	100
	^{228}Th	30 ± 2.1	2.1 ± 0.6	82 ± 23	37	1.8 ± 0.9	70 ± 35	30	1.5 ± 0.6	73 ± 29	33	0	0

n.d.: not detected

Table A-14: Extracted portions from the uranium samples U-ST-1, U-ST-2 and U-ST-3; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR			3. BCR			
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
U-ST-1, <0.1mm	^{238}U	185 ± 21	11 ± 5.5	443 ± 216	44	14.2 ± 5.6	558 ± 220	56	n.d.	-/-	-/-	0	0
	^{226}Ra	152 ± 10	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	152	100
	^{214}Pb	160 ± 11	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	160	100
	^{214}Bi	144 ± 9.4	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	144	100
	^{210}Pb	163 ± 25	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	163	100
	^{228}Ra	32 ± 3.6	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	32	100
	^{228}Th	31 ± 3	2 ± 0.8	79 ± 31	34	1.8 ± 1.8	71 ± 71	30	1.7 ± 1.7	83 ± 83	36	0	0
U-ST-2, <0.1mm	^{238}U	141 ± 28	n.d.	-/-	-/-	5.1 ± 4	199 ± 155	100	n.d.	-/-	-/-	0	0
	^{226}Ra	142 ± 8.6	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	142	100
	^{214}Pb	140 ± 7.5	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	140	100
	^{214}Bi	144 ± 9.6	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	144	100
	^{210}Pb	155 ± 37	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	155	100
	^{228}Ra	40 ± 4.2	1.4 ± 1	54 ± 39	22	2.7 ± 0.9	103 ± 35	42	1.9 ± 0.8	87 ± 37	36	0	0
	^{228}Th	36 ± 3.3	1.7 ± 0.8	68 ± 29	38	2.1 ± 0.8	83 ± 30	44	0.7 ± 0.6	33 ± 26	18	0	0
U-ST-3, <0.1mm	^{238}U	1088 ± 316	5.5 ± 4.1	202 ± 150	18	n.d.			19 ± 7.6	878 ± 343	82	0	0
	^{226}Ra	2098 ± 122	2.6 ± 0.5	94 ± 18	5	3.6 ± 0.5	135 ± 19	7	13 ± 0.8	607 ± 44	29	1261	60
	^{214}Pb	2085 ± 106	2.8 ± 0.4	103 ± 14	5	4 ± 0.4	151 ± 17	7	15 ± 0.7	674 ± 32	32	1157	56
	^{214}Bi	2111 ± 138	2.4 ± 0.6	86 ± 23	4	3.1 ± 0.6	120 ± 21	6	12 ± 0.8	539 ± 36	26	1366	65
	^{210}Pb	1424 ± 124	n.d.	-/-	-/-	n.d.	-/-	-/-	18 ± 4.6	793 ± 208	28	2055	72
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{228}Th	10 ± 3.6	2.5 ± 0.8	91 ± 30	43	1.6 ± 1.2	62 ± 46	28	1.4 ± 0.7	62 ± 32	29	0	0

n.d.: not detected

Table A-15: Extracted portions from the uranium samples U-ST-4, U-S-5 and U-S-6; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions										residual activity concentration	
			1. BCR			2. BCR			3. BCR					
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]		[Bq/kg]	[%]
U-ST-4, <0.1mm	^{238}U	82,968 ± 5227	105 ± 37	3888 ± 1359	6	26 ± 6.6	964 ± 249	1	1051 ± 363	47,906 ± 16,546	69		16,380	24
	^{226}Ra	124,400 ± 8162	34 ± 1.4	1244 ± 52	1	103 ± 3.5	3896 ± 130	3	1109 ± 33	50,574 ± 1504	40		68,687	55
	^{214}Pb	126,100 ± 8747	37 ± 1.4	1354 ± 52	1	114 ± 3.6	4289 ± 136	3	1199 ± 34	54,653 ± 1564	43		65,803	52
	^{214}Bi	122,700 ± 7577	31 ± 1.4	1134 ± 52	1	93 ± 3.3	3502 ± 125	3	1020 ± 32	46,493 ± 1445	38		71,570	58
	^{210}Pb	84,880 ± 4332	30 ± 6.6	1107 ± 245	1	14 ± 5.7	515 ± 215	0.6	1555 ± 149	70,880 ± 6792	84		12,377	15
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-		-/-	-/-
	^{228}Th	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-		-/-	-/-
U-S-5, <2mm	^{238}U	64 ± 15	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-		64	100
	^{226}Ra	60 ± 5	n.d.	-/-	-/-	1.4 ± 1	54 ± 39	65	0.6 ± 0.3	29 ± 14	35		0	0
	^{214}Pb	55 ± 4.2	n.d.	-/-	-/-	0.8 ± 0.5	31 ± 19	52	0.6 ± 0.2	29 ± 9.5	48		0	0
	^{214}Bi	64 ± 5.7	n.d.	-/-	-/-	2 ± 1.5	77 ± 58	73	0.6 ± 0.4	29 ± 19	27		0	0
	^{210}Pb	66 ± 20	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-		66	100
	^{228}Ra	11 ± 7	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-		11	100
	^{228}Th	13 ± 1.6	2.1 ± 0.9	80 ± 34	30	2.7 ± 1.2	104 ± 46	38	1.8 ± 0.6	86 ± 29	32		0	0
U-S-6, <2mm	^{238}U	842 ± 74	n.d.	-/-	-/-	n.d.	-/-	-/-					842	100
	^{226}Ra	830 ± 61	1.7 ±	65 ±	8	7.1 ±	278 ±	34					486	58
	^{214}Pb	765 ± 53	1.4 ±	54 ±	7	7.2 ±	282 ±	37		sample			429	56
	^{214}Bi	894 ± 68	2 ±	77 ±	9	7 ±	275 ±	31					543	61
	^{210}Pb	764 ± 68	n.d.	-/-	-/-	n.d.	-/-	-/-		lost			764	100
	^{228}Ra	28 ± 7.8	n.d.	-/-	-/-	n.d.	-/-	-/-					28	100
	^{228}Th	26 ± 5.7	1.5 ±	58 ±	45	1.8 ±	71 ±	55					0	0

n.d.: not detected

A-3-a Milled samples

Table A-16: Extracted portions from the aluminium samples R-AO-1, R-AO-2 and W-RS-1; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
R-AO-1, <0.1mm	^{238}U	130 ± 19	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	130	100
	^{226}Ra	231 ± 17	11 ± 1.1	442 ± 42	63	5 ± 1	194 ± 38	26	1.5 ± 0.8	73 ± 40	11	0	0
	^{214}Pb	216 ± 15	11 ± 1	430 ± 40	63	5 ± 0.9	188 ± 36	26	1.5 ± 0.7	75 ± 35	11	0	0
	^{214}Bi	245 ± 19	11 ± 1.1	454 ± 44	63	5 ± 1	200 ± 40	27	1.4 ± 0.9	70 ± 45	10	0	0
	^{210}Pb	422 ± 38	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	422	100
	^{228}Ra	176 ± 16	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	176	100
	^{228}Th	156 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	156	100
R-AO-2, <0.1mm	^{238}U	862 ± 72	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	862	100
	^{226}Ra	2182 ± 159	34 ± 1.3	1275 ± 50	41	42 ± 1.4	1613 ± 54	51	5.7 ± 0.9	274 ± 43	8	0	0
	^{214}Pb	2000 ± 137	34 ± 1.3	1294 ± 50	41	42 ± 1.4	1632 ± 54	51	6 ± 0.9	288 ± 43	8	0	0
	^{214}Bi	2363 ± 180	33 ± 1.3	1256 ± 50	41	41 ± 1.4	1593 ± 54	51	5.4 ± 0.9	260 ± 43	8	0	0
	^{210}Pb	3927 ± 293	27 ± 5.3	1028 ± 202	26	11 ± 5.3	435 ± 206	11	n.d.	-/-	-/-	2465	63
	^{228}Ra	169 ± 17	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	169	100
	^{228}Th	147 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	147	100
W-RS-1, <0.1mm	^{238}U	191 ± 26	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	191	100
	^{226}Ra	195 ± 15	6.2 ± 1	252 ± 39	24	3.3 ± 0.7	137 ± 27	13	12 ± 1	649 ± 52	63	0	0
	^{214}Pb	186 ± 13	5.6 ± 0.9	229 ± 37	23	2.9 ± 0.6	122 ± 25	12	12 ± 1	643 ± 52	64	0	0
	^{214}Bi	203 ± 16	6.7 ± 1	274 ± 41	26	3.6 ± 0.7	152 ± 30	13	12 ± 1	654 ± 52	61	0	0
	^{210}Pb	329 ± 39	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	329	100
	^{228}Ra	516 ± 43	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	516	100
	^{228}Th	459 ± 36	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	459	100

n.d.: not detected

Table A-17: Extracted portions from the uranium samples W-T-1, W-T-2 and W-T-3; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR		3. BCR				
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
W-T-1, <0.1mm	^{238}U	1553 ± 246	7 ± 4.8	271 ± 185	17	9.4 ± 4.7	367 ± 183	24	n.d.	-/-	-/-	916	59
	^{226}Ra	4691 ± 280	30 ± 1.3	1168 ± 50	25	27 ± 1.2	1058 ± 47	23	7.1 ± 0.6	343 ± 27	7	2121	45
	^{214}Pb	4571 ± 289	34 ± 1.3	1290 ± 50	28	30 ± 1.2	1177 ± 47	26	7.8 ± 0.5	377 ± 24	8	1727	38
	^{214}Bi	4810 ± 271	27 ± 1.3	1046 ± 50	22	24 ± 1.2	939 ± 47	20	6.4 ± 0.6	310 ± 29	6	2516	52
	^{210}Pb	9189 ± 748	50 ± 6.7	1926 ± 258	21	16 ± 4.8	630 ± 187	7	12 ± 3.8	578 ± 184	6	6055	66
	^{228}Ra	31 ± 3.3	2.9 ± 1.1	113 ± 42	100	n.d.	-/-	-/-	n.d.	-/-	-/-	0	0
	^{228}Th	32 ± 2.7	3.4 ± 1.2	131 ± 46	47	1.5 ± 0.9	58 ± 35	20	1.9 ± 0.6	91 ± 29	33	0	0
W-T-2, <0.1mm	^{238}U	1875 ± 297	10 ± 5.7	391 ± 216	21	23 ± 5.9	897 ± 231	48	4.9 ± 3	239 ± 146	13	348	19
	^{226}Ra	5556 ± 332	36 ± 1.5	1381 ± 55	25	56 ± 2	2178 ± 78	39	8.3 ± 0.6	403 ± 27	7	1594	29
	^{214}Pb	5433 ± 344	39 ± 1.4	1472 ± 53	27	61 ± 2	2379 ± 78	44	8.9 ± 0.5	434 ± 24	8	1148	21
	^{214}Bi	5678 ± 320	34 ± 1.5	1290 ± 57	23	51 ± 2	1977 ± 78	35	7.6 ± 0.6	371 ± 29	7	2040	36
	^{210}Pb	10,260 ± 833	48 ± 7.2	1823 ± 273	18	25 ± 5.7	997 ± 223	10	9.5 ± 3.8	464 ± 185	5	6979	68
	^{228}Ra	29 ± 3.2	1.4 ± 0.9	54 ± 34	100	n.d.	-/-	-/-	n.d.	-/-	-/-	0	0
	^{228}Th	27 ± 2.4	1 ± 0.9	39 ± 34	22	1.7 ± 0.9	67 ± 35	37	1.5 ± 0.6	73 ± 29	41	0	0
W-T-3, <0.1mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	-/-	-/-
	^{226}Ra	9754 ± 583	2.3 ± 0.7	88 ± 210	0.9	142 ± 4.6	5575 ± 180	57	16 ± 0.8	797 ± 39	8	3294	34
	^{214}Pb	9601 ± 607	2.1 ± 0.6	82 ± 25	0.8	153 ± 4.7	6002 ± 184	63	18 ± 0.8	872 ± 39	9	2646	28
	^{214}Bi	9907 ± 558	2.4 ± 0.7	94 ± 23	0.9	132 ± 4.5	5148 ± 176	52	15 ± 0.8	722 ± 39	7	3942	40
	^{210}Pb	15,910 ± 1291	56 ± 7.8	2171 ± 27	14	66 ± 9.3	2577 ± 364	16	15 ± 4.1	735 ± 201	5	10,427	66
	^{228}Ra	33 ± 4	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	33	100
	^{228}Th	31 ± 3	1.8 ± 0.9	72 ± 35	36	1.6 ± 0.9	63 ± 35	32	1.3 ± 0.6	65 ± 29	33	0	0

n.d.: not detected

Table A-18: Extracted portions from the uranium samples W-T-4, U-S-5 and U-S-6; given error quotes to 2σ-reliability.

samples		initial specific activity	BCR extraction fractions								residual activity concentration	
			1. BCR			2. BCR			3. BCR			
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]	[Bq/kg]	[%]
W-T-4, <0.1mm	^{238}U	1773 ± 280	7.5 ± 4.6	285 ± 174	16	7.2 ± 5.4	280 ± 209	16	5.2 ± 3.6	254 ± 175	14	954	54
	^{226}Ra	3011 ± 180	12 ± 0.8	462 ± 30	15	28 ± 1.3	1094 ± 48	36	7 ± 0.6	327 ± 27	11	1128	37
	^{214}Pb	2955 ± 187	14 ± 0.8	510 ± 30	17	31 ± 1.2	1185 ± 47	40	7.4 ± 0.5	358 ± 24	12	903	31
	^{214}Bi	3066 ± 173	11 ± 0.8	413 ± 30	14	26 ± 1.3	1004 ± 50	33	6.1 ± 0.6	296 ± 29	10	1353	44
	^{210}Pb	7844 ± 639	28 ± 5.5	1040 ± 208	13	18 ± 5.1	683 ± 198	9	8.6 ± 3.5	417 ± 170	5	5705	73
	^{228}Ra	28 ± 2.5	n.d.	-/-	-/-	2.3 ± 1.2	87 ± 47	100	n.d.	-/-	-/-	0	0
	^{228}Th	30 ± 2.1	1.9 ± 0.9	71 ± 34	32	2.3 ± 0.9	89 ± 35	41	1.2 ± 0.6	61 ± 29	27	0	0
U-S-5, <0.1mm	^{238}U	64 ± 15	33 ± 4.5	1226 ± 169	47	9.6 ± 3.8	379 ± 150	15	21 ± 3.5	1017 ± 170	38	0	0
	^{226}Ra	60 ± 5	11 ± 0.8	428 ± 28	24	17 ± 0.9	669 ± 34	38	14 ± 0.8	669 ± 37	38	0	0
	^{214}Pb	55 ± 4.2	12 ± 0.7	465 ± 26	24	19 ± 0.8	730 ± 32	38	15 ± 0.7	725 ± 34	38	0	0
	^{214}Bi	64 ± 5.7	10 ± 0.8	390 ± 30	24	15 ± 0.9	608 ± 35	38	13 ± 0.8	613 ± 39	38	0	0
	^{210}Pb	66 ± 20	34 ± 6.2	1260 ± 233	48	30 ± 5.6	1189 ± 221	46	3 ± 2	146 ± 97	6	0	0
	^{228}Ra	11 ± 7	n.d.	-/-	-/-	n.d.	-/-	-/-	13 ± 1	628 ± 48	100	0	0
	^{228}Th	13 ± 1.6	2.4 ± 0.9	90 ± 34	41	1.5 ± 0.9	59 ± 36	26	1.5 ± 0.6	73 ± 29	33	0	0
U-S-6, <0.1mm	^{238}U	842 ± 74	7.1 ± 3.3	271 ± 126	25	7.4 ± 3.1	290 ± 121	27	11 ± 3	531 ± 146	48	0	0
	^{226}Ra	830 ± 61	2.1 ± 0.6	78 ± 21	7	14 ± 0.8	539 ± 29	49	9.9 ± 0.6	482 ± 29	44	0	0
	^{214}Pb	765 ± 53	1.7 ± 0.4	65 ± 15	7	15 ± 0.7	576 ± 27	49	11 ± 0.6	521± 29	44	0	0
	^{214}Bi	894 ± 68	2.4 ± 0.7	92 ± 27	9	13 ± 0.8	501 ± 31	48	9.1 ± 0.6	443 ± 29	43	0	0
	^{210}Pb	764 ± 68	11 ± 4.5	408 ± 172	32	7.5 ± 4.3	294 ± 169	22	12 ± 3.9	585 ± 190	46	0	0
	^{228}Ra	28 ± 7.8	n.d.	-/-	-/-	n.d.	-/-	-/-	n.d.	-/-	-/-	28	100
	^{228}Th	26 ± 5.7	2.1 ± 0.9	80 ± 34	43	1.2 ± 35	47 ± 35	25	1.2 ± 0.6	59 ± 29	32	0	0

n.d.: not detected

A-4 Radionuclide portions extracted by DIN 19730 and DIN 38414/S4 procedures

Table A-19: Extracted portions from the phosphate samples R-PO-1, R-PO-2, W-PG-1, P-F-1, P-F-2 and the aluminium sample R-AO-1; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
R-PO-1, <2mm	^{238}U	1484 ± 100	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	1479 ± 98	11 ± 0.8	25 ± 1.8	2	n.d.	-/-	-/-
	^{214}Pb	1556 ± 107	12 ± 0.7	26 ± 1.6	2	n.d.	-/-	-/-
	^{214}Bi	1402 ± 88	10 ± 0.9	23 ± 2	2	n.d.	-/-	-/-
	^{210}Pb	1603 ± 91	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	18 ± 4.8	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	15 ± 3.3	2.7 ± 0.9	6.1 ± 2	41	2.4 ± 0.9	22 ± 8.4	100
R-PO-2, <2mm	^{238}U	19 ± 7.8	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	31 ± 2.4	0.8 ± 0.5	1.7 ± 1	6	n.d.	-/-	-/-
	^{214}Pb	32 ± 2.5	0.8 ± 0.4	1.7 ± 0.8	5	n.d.	-/-	-/-
	^{214}Bi	29 ± 2.3	0.8 ± 0.5	1.7 ± 1.1	6	n.d.	-/-	-/-
	^{210}Pb	15 ± 7.1	6.3 ± 4.1	13 ± 8.7	45	n.d.	-/-	-/-
	^{228}Ra	80 ± 6.4	1.5 ± 1.2	3.2 ± 2.5	4	n.d.	-/-	-/-
	^{228}Th	86 ± 6	2.1 ± 0.9	4.4 ± 1.9	6	2.1 ± 0.9	20 ± 8.5	26
W-PG-1, <2mm	^{238}U	40 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	41 ± 3.5	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{214}Pb	43 ± 3.5	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{214}Bi	39 ± 3.5	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{210}Pb	41 ± 13	26 ± 0.7	40 ± 1.1	97	n.d.	-/-	-/-
	^{228}Ra	60 ± 7	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	50 ± 5.1	3 ± 1.2	4.7 ± 1.9	9	2.7 ± 1.2	19 ± 8.6	38
P-F-1, <2mm	^{238}U	842 ± 56	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	149 ± 11	1.4 ± 0.6	3.2 ± 1.4	2	n.d.	-/-	-/-
	^{214}Pb	160 ± 12	1.5 ± 0.5	3.6 ± 1.2	2	n.d.	-/-	-/-
	^{214}Bi	137 ±10	1.2 ± 0.7	2.9 ± 1.7	2	n.d.	-/-	-/-
	^{210}Pb	164 ± 27	11 ± 6.3	26 ± 15	16	n.d.	-/-	-/-
	^{228}Ra	14 ± 6.8	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	7 ± 1.1	2.4 ± 0.9	5.8 ± 2.2	84	1.5 ± 0.9	14 ± 8.6	100
P-F-2, <2mm	^{238}U	846 ± 54	138 ± 9.7	346 ± 24	45	24 ± 4.3	220 ± 39	29
	^{226}Ra	275 ± 19	1.2 ± 0.5	3 ± 1.3	1	0.8 ± 0.5	7.3 ± 4.6	3
	^{214}Pb	290 ± 20	1.4 ± 0.4	3.5 ± 1	1	0.7 ± 0.4	6.4 ± 3.7	2
	^{214}Bi	259 ± 17	1 ± 0.6	2.5 ± 1.5	1	0.9 ± 0.6	8.2 ± 5.5	3
	^{210}Pb	268 ± 25	42 ± 7.7	105 ± 19	33	n.d.	-/-	-/-
	^{228}Ra	<11	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	<6.9	n.d.	-/-	-/-	n.d.	-/-	-/-
R-AO-1, <2mm	^{238}U	130 ± 19	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	231 ± 17	40 ± 2.2	85 ± 4.6	37	5 ± 1.1	51 ± 10	22
	^{214}Pb	216 ± 15	39 ± 2.1	83 ± 4.4	38	4.9 ± 1	47 ± 9.5	22
	^{214}Bi	245 ± 19	41 ± 2.3	87 ± 4.9	35	5.8 ± 1.1	55 ± 11	23
	^{210}Pb	423 ± 38	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	176 ± 16	5.1 ± 2	11 ± 4.2	6	n.d.	-/-	-/-
	^{228}Th	156 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-

n.d.: not detected

Table A-20: Extracted portions from the aluminium samples R-AO-2 and W-RS-1 and the refractory samples R-ZS-1, W-FD-1, P-FZM-1 and P-FZM-2; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
R-AO-2, <2mm	^{238}U	862 ± 72	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	2182 ± 159	390 ± 11	802 ± 22	37	3.9 ± 0.7	37 ± 6.6	2
	^{214}Pb	2000 ± 137	401 ± 11	825 ± 23	41	3.7 ± 0.7	35 ± 6.6	2
	^{214}Bi	2363 ± 180	379 ± 10	780 ± 21	33	4.1 ± 0.7	39 ± 6.6	2
	^{210}Pb	3928 ± 293	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	169 ± 17	6.2 ± 3.2	13 ± 6.6	8	n.d.	-/-	-/-
	^{228}Th	147 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-
W-RS-1, <2mm	^{238}U	191 ± 26	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	195 ± 15	2 ± 1	4 ± 1.8	2	8 ± 1.1	73 ± 9.6	37
	^{214}Pb	186 ± 13	1.7 ± 1	3.3 ± 1.9	2	7.6 ± 1	70 ± 9.2	37
	^{214}Bi	203 ± 16	2 ± 0.9	3.8 ± 17	2	8.3 ± 1.1	76 ± 10	37
	^{210}Pb	329 ± 39	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	516 ± 43	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	459 ± 36	n.d.	-/-	-/-	n.d.	-/-	-/-
R-ZS-1, <2mm	^{238}U	2575 ± 222	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	2930 ± 215	1 ± 0.4	2 ± 0.9	0.1	n.d.	-/-	-/-
	^{214}Pb	2610 ± 179	1.1 ± 0.3	2.5 ± 0.7	0.1	n.d.	-/-	-/-
	^{214}Bi	3249 ± 250	0.9 ± 0.5	2 ± 1.1	0.1	n.d.	-/-	-/-
	^{210}Pb	2610 ± 288	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	762 ± 61	2 ± 1.2	4.5 ± 2.7	0.6	n.d.	-/-	-/-
	^{228}Th	690 ± 53	2.4 ± 0.9	5.4 ± 2	0.8	2.1 ± 0.9	18 ± 7.8	3
W-FD-1, <0.1mm	^{238}U	289 ± 68	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	295 ± 23	1.8 ± 1	6.8 ± 3.6	2	n.d.	-/-	-/-
	^{214}Pb	283 ± 21	1 ± 0.4	3.8 ± 1.5	1	n.d.	-/-	-/-
	^{214}Bi	306 ± 26	2.6 ± 1.5	9.8 ± 5.7	3	n.d.	-/-	-/-
	^{210}Pb	162,400 ± 14,260	293 ± 29	1105 ± 107	0.7	6.5 ± 4.2	57 ± 37	0.1
	^{228}Ra	74 ± 18	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	80 ± 13	2.1 ± 0.9	7.9 ± 3.4	10	1.8 ± 0.9	5.2 ± 7.8	19
P-FZM-1, <2mm	^{238}U	1829 ± 129	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	1601 ± 106	1 ± 0.5	2.1 ± 1.1	0.1	n.d.	-/-	-/-
	^{214}Pb	1680 ± 116	1.1 ± 0.4	2.3 ± 0.8	0.1	n.d.	-/-	-/-
	^{214}Bi	1522 ± 96	0.9 ± 0.6	1.9 ± 1.3	0.1	n.d.	-/-	-/-
	^{210}Pb	932 ± 92	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	388 ± 26	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	369 ± 25	1.8 ± 0.9	3.8 ± 1.9	1	2.4 ± 0.9	21 ± 7.8	6
P-FZM-2, <0.1mm	^{238}U	3913 ± 260	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	4206 ± 278	4.1 ± 0.6	8.8 ± 1.3	0.2	n.d.	-/-	-/-
	^{214}Pb	4421 ± 306	4.2 ± 0.6	9.1 ± 1.1	0.2	n.d.	-/-	-/-
	^{214}Bi	3990 ± 249	3.9 ± 0.7	8.5 ± 1.5	0.2	n.d.	-/-	-/-
	^{210}Pb	950 ± 124	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	853 ± 55	2.2 ± 1.3	4.8 ± 2.8	0.6	n.d.	-/-	-/-
	^{228}Th	780 ± 52	3 ± 0.9	6.5 ± 2	0.8	2.1 ± 0.9	19 ± 8.2	2

n.d.: not detected

Table A-21: Extracted portions from the crude oil exploitation samples W-SL-1, W-SL-2, W-SC-1 and W-SC-2 and the thorium samples U-SO-1 and U-SO-2; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
W-SL-1, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	17,570 ± 1287	16 ± 0.9	29 ± 1.7	0.2	2.1 ± 0.6	15 ± 4	0.1
	^{214}Pb	16,010 ± 1092	17 ± 0.8	32 ± 1.5	0.2	1.8 ± 0.4	13 ± 2.9	0.1
	^{214}Bi	19,130 ± 1481	14 ± 1	27 ± 1.9	0.1	2.4 ± 0.7	18 ± 5.1	0.1
	^{210}Pb	27,048 ± 2405	7.4 ± 5	14 ± 9.4	0.1	n.d.	-/-	-/-
	^{228}Ra	3832 ± 303	5.1 ± 1.4	9.6 ± 2.6	0.3	n.d.	-/-	-/-
	^{228}Th	4185 ± 315	1.8 ± 0.9	3.4 ± 1.7	0.1	2.1 ± 0.9	15 ± 6.5	0.4
W-SL-2, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	48,100 ± 3526	29 ± 1.3	55 ± 2.5	0.1	2.1 ± 0.5	17 ± 4.1	0.1
	^{214}Pb	44,120 ± 3007	31 ± 1.2	60 ± 2.3	0.1	2.4 ± 0.4	20 ± 3.3	0.1
	^{214}Bi	52,080 ± 4045	27 ± 1.4	51 ± 2.7	0.1	1.7 ± 0.6	14 ± 5	0.1
	^{210}Pb	46,125 ± 4108	9.2 ± 5.5	18 ± 11	0.1	n.d.	-/-	-/-
	^{228}Ra	12,840 ± 1006	9 ± 1.7	17 ± 3.2	0.1	1.3 ± 1.2	11 ± 9.9	0.1
	^{228}Th	13,020 ± 978	3 ± 1.2	5.7 ± 2.3	0.1	2.1 ± 0.9	17 ± 7.4	0.1
W-SC-1, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	3705 ± 270	1.2 ± 0.5	2.2 ± 1	0.1	n.d.	-/-	-/-
	^{214}Pb	3378 ± 231	1.4 ± 0.4	2.7 ± 0.8	0.1	n.d.	-/-	-/-
	^{214}Bi	4032 ± 309	0.9 ± 0.6	1.7 ± 1.1	0.1	n.d.	-/-	-/-
	^{210}Pb	44,821 ± 3954	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	1162 ± 93	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	1335 ± 101	n.d.	-/-	-/-	1.5 ± 0.9	9.9 ± 5.9	0.7
W-SC-2, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	9235 ± 677	5.2 ± 0.7	10 ± 1.4	0.1	n.d.	-/-	-/-
	^{214}Pb	8279 ± 565	6.4 ± 0.6	13 ± 1.2	0.2	n.d.	-/-	-/-
	^{214}Bi	10,190 ± 788	4 ± 0.8	7.8 ± 1.6	0.1	n.d.	-/-	-/-
	^{210}Pb	45,559 ± 4011	n.d.	-/-	-/-	13.8 ± 4.4	112 ± 36	0.2
	^{228}Ra	1427 ± 114	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	1794 ± 135	1.5 ± 0.9	2.9 ± 1.8	0.2	2.1 ± 0.9	17 ± 7.3	1
U-SO-1, <2mm	^{238}U	16,112 ± 3102	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	1024 ± 249	3.4 ± 2.1	6.3 ± 3.8	0.7	n.d.	-/-	-/-
	^{214}Pb	733 ± 204	3.7 ± 2.4	6.8 ± 4.4	0.9	n.d.	-/-	-/-
	^{214}Bi	1314 ± 293	3.1 ± 1.7	5.7 ± 3.1	0.4	n.d.	-/-	-/-
	^{210}Pb	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	501,400 ± 39,160	2711 ± 75	4984 ± 137	1	11 ± 1	79 ± 7.3	0.1
	^{228}Th	417,000 ± 31,350	167 ± 6.9	306 ± 13	0.1	3 ± 0.6	22 ± 4.4	0.1
U-SO-2, <2mm	^{238}U	2398 ± 206	14 ± 6.3	28 ± 13	1	n.d.	-/-	-/-
	^{226}Ra	1197 ± 88	2.5 ± 1.4	5 ± 2.8	0.4	n.d.	-/-	-/-
	^{214}Pb	1100 ± 76	2.7 ± 1.3	5.4 ± 2.6	0.5	n.d.	-/-	-/-
	^{214}Bi	1293 ± 99	2.3 ± 1.5	4.6 ± 3	0.4	n.d.	-/-	-/-
	^{210}Pb	1963 ± 215	9.7 ± 7.3	20 ± 15	1	n.d.	-/-	-/-
	^{228}Ra	10,960 ± 857	295 ± 25	594 ± 50	5	n.d.	-/-	-/-
	^{228}Th	9279 ± 699	27 ± 2.4	54 ± 4.8	0.6	n.d.	-/-	-/-

n.d.: not detected

Table A-22: Extracted portions from the thorium samples U-SO-3 and U-SO-4 and the uranium samples W-T-1, W-T-2, W-T-3 and W-T-4; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
U-SO-3, <2mm	^{238}U	1762 ± 163	28 ± 6.2	62 ± 14	4	n.d.	-/-	-/-
	^{226}Ra	880 ± 65	12 ± 0.9	27 ± 2	3	n.d.	-/-	-/-
	^{214}Pb	814 ± 57	12 ± 0.8	27 ± 1.8	3	n.d.	-/-	-/-
	^{214}Bi	945 ± 73	12 ± 1	27 ± 2.2	3	n.d.	-/-	-/-
	^{210}Pb	1596 ± 179	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	8915 ± 697	258 ± 8.3	569 ± 18	6	2.4 ± 1.2	23 ± 11	0.3
	^{228}Th	7599 ± 573	20 ± 1.8	43 ± 4	0.6	2.1 ± 0.9	20 ± 8.6	0.3
U-SO-4, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	18 ± 2.1	1.1 ± 0.5	2.3 ± 1	14	0.8 ± 0.5	5.7 ± 3.4	32
	^{214}Pb	16 ± 1.6	1.2 ± 0.3	2.7 ± 0.7	17	0.7 ± 0.4	5.3 ± 3	34
	^{214}Bi	20 ± 2.5	0.9 ± 0.6	2 ± 1.3	10	0.8 ± 0.5	6.1 ± 3.8	30
	^{210}Pb	38 ± 17	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	37 ± 4.5	n.d.	-/-	-/-	2.4 ± 0.9	18 ± 6.8	50
W-T-1, <2mm	^{238}U	1553 ± 246	24 ± 7.8	48 ± 16	3	n.d.	-/-	-/-
	^{226}Ra	4691 ± 280	615 ± 19	1252 ± 38	27	9.7 ± 0.7	91 ± 6.6	2
	^{214}Pb	4571 ± 289	662 ± 19	1346 ± 39	30	9.7 ± 0.6	91 ± 5.6	2
	^{214}Bi	4810 ± 271	569 ± 18	1157 ± 37	24	9.7 ± 0.8	91 ± 7.5	2
	^{210}Pb	9189 ± 748	48 ± 11	97 ± 22	1	n.d.	-/-	-/-
	^{228}Ra	31 ± 3.3	n.d.	-/-	-/-	2 ± 0.9	19 ± 8.5	60
	^{228}Th	32 ± 2.7	3.1 ± 1.5	6.3 ± 3.1	20	1.2 ± 0.9	11 ± 8.5	35
W-T-2, <2mm	^{238}U	1875 ± 297	56 ± 10	117 ± 22	6	9.3 ± 6.4	89 ± 61	5
	^{226}Ra	5556 ± 332	627 ± 17	1309 ± 35	24	6.7 ± 0.6	64 ± 5.7	1
	^{214}Pb	5433 ± 344	677 ± 17	1415 ± 36	26	6.7 ± 0.5	64 ± 4.8	1
	^{214}Bi	5678 ± 320	576 ± 16	1204 ± 33	21	6.7 ± 0.7	64 ± 6.7	1
	^{210}Pb	10,260 ± 833	71 ± 13	148 ± 27	1	n.d.	-/-	-/-
	^{228}Ra	29 ± 3.2	n.d.	-/-	-/-	2.3 ± 0.8	22 ± 7.6	76
	^{228}Th	27 ± 2.4	2.7 ± 1.2	5.6 ± 2.5	21	1.8 ± 0.9	17 ± 8.6	63
W-T-3, <2mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	9754 ± 583	218 ± 6.2	418 ± 23	4	5.4 ± 0.6	51 ± 5.3	1
	^{214}Pb	9601 ± 607	235 ± 6.3	450 ± 12	5	6 ± 0.5	58 ± 4.8	0.6
	^{214}Bi	9907 ± 558	201 ± 6.1	385 ± 12	4	4.7 ± 0.6	45 ± 5.7	0.5
	^{210}Pb	15,910 ± 1291	89 ± 12	170 ± 12	1	n.d.	-/-	-/-
	^{228}Ra	33 ± 4	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	31 ± 3	3.9 ± 1.5	7.5 ± 2.9	24	n.d.	-/-	-/-
W-T-4, <2mm	^{238}U	1773 ± 280	62 ± 8.1	127 ± 17	7	n.d.	-/-	-/-
	^{226}Ra	3011 ± 180	216 ± 6.1	441 ± 13	15	2.2 ± 0.5	21 ± 4.8	1
	^{214}Pb	2955 ± 187	233 ± 6.2	476 ± 13	16	2.3 ± 0.4	22 ± 3.8	0.7
	^{214}Bi	3066 ± 173	198 ± 6	404 ± 12	13	2 ± 0.6	19 ± 5.7	0.6
	^{210}Pb	7844 ± 639	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	28 ± 2.5	n.d.	-/-	-/-	1.9 ± 1	18 ± 9.6	65
	^{228}Th	30 ± 2.1	1.5 ± 1.2	3.1 ± 2.5	10	2.1 ± 0.9	20 ± 8.6	68

n.d.: not detected

Table A-23: Extracted portions from the uranium samples U-ST-1, U-ST-2, U-ST-3 and U-ST-4 and U-S-5 and U-S-6; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
U-ST-1, <0.1mm	^{238}U	185 ± 21	5.6 ± 4.4	12 ± 9.6	12	9.4 ± 6	89 ± 57	48
	^{226}Ra	152 ± 10	0.8 ± 0.4	1.8 ± 0.8	1	8.9 ± 0.7	84 ± 7	55
	^{214}Pb	160 ± 11	0.7 ± 0.4	1.5 ± 0.8	0.9	10 ± 0.7	98 ± 6.6	61
	^{214}Bi	144 ± 9.4	0.9 ± 0.4	2.1 ± 0.9	1	7.4 ± 0.8	70 ± 7.4	49
	^{210}Pb	163 ± 25	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	32 ± 3.6	n.d.	-/-	-/-	2.1 ± 1	20 ± 9.4	63
	^{228}Th	31 ± 3	1.9 ± 0.8	4.1 ± 1.8	14	1.5 ± 0.6	14 ± 5.7	46
U-ST-2, <0.1mm	^{238}U	141 ± 28	n.d.	-/-	-/-	6 ± 3.7	57 ± 35	40
	^{226}Ra	142 ± 8.6	0.8 ± 0.4	1.9 ± 0.8	1	n.d.	-/-	-/-
	^{214}Pb	140 ± 7.5	0.7 ± 0.3	1.6 ± 0.7	1	n.d.	-/-	-/-
	^{214}Bi	144 ± 9.6	1 ± 0.4	2.2 ± 0.9	2	n.d.	-/-	-/-
	^{210}Pb	155 ± 37	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	40 ± 4.2	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	36 ± 3.3	2.2 ± 1.1	5 ± 2.5	14	2.4 ± 0.8	23 ± 7.9	63
U-ST-3, <0.1mm	^{238}U	1088 ± 316	56 ± 9.7	119 ± 21	13	n.d.	-/-	-/-
	^{226}Ra	2098 ± 122	126 ± 4.2	268 ± 8.9	13	n.d.	-/-	-/-
	^{214}Pb	2085 ± 106	136 ± 4.2	289 ± 8.9	14	n.d.	-/-	-/-
	^{214}Bi	2111 ± 138	116 ± 4.2	247 ± 8.9	12	n.d.	-/-	-/-
	^{210}Pb	1423 ± 124	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.		
	^{228}Th	10 ± 3.6	3.2 ± 1.2	6.8 ± 2.6	67	2.4 ± 0.9	23 ± 8.5	100
U-ST-4, <0.1mm	^{238}U	82,968 ± 5227	2085 ± 115	4427 ± 244	6	n.d.	-/-	-/-
	^{226}Ra	124,400 ± 8162	2334 ± 59	4955 ± 125	4	3.3 ± 0.4	31 ± 3.3	0.1
	^{214}Pb	126,100 ± 8747	2508 ± 62	5326 ± 131	4	2.5 ± 0.3	24 ± 2.8	0.1
	^{214}Bi	122,700 ± 7577	2159 ± 56	4584 ± 120	4	4.1 ± 0.4	39 ± 3.8	0.1
	^{210}Pb	84880 ± 4332	100 ± 21	212 ± 45	0.4	n.d.	-/-	-/-
	^{228}Ra	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
U-S-5, <2mm	^{238}U	64 ± 15	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	60 ± 5	1.1 ± 0.6	2.1 ± 1.1	4	n.d.	-/-	-/-
	^{214}Pb	55 ± 4.2	1.3 ± 0.4	2.5 ± 0.4	5	n.d.	-/-	-/-
	^{214}Bi	64 ± 5.7	0.9 ± 0.7	1.7 ± 0.7	3	n.d.	-/-	-/-
	^{210}Pb	66 ± 20	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	11 ± 7	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	13 ± 1.6	2.4 ± 0.9	4.6 ± 1.7	12	2.1 ± 0.9	19 ± 8.2	49
U-S-6, <2mm	^{238}U	842 ± 74	6.6 ± 4.6	12 ± 8.6	2	n.d.	-/-	-/-
	^{226}Ra	830 ± 61	6.8 ± 0.8	13 ± 1.5	2	n.d.	-/-	-/-
	^{214}Pb	765 ± 53	8.5 ± 0.7	16 ± 1.3	2	n.d.	-/-	-/-
	^{214}Bi	894 ± 68	5.1 ± 0.9	9.5 ± 1.7	1	n.d.	-/-	-/-
	^{210}Pb	764 ± 68	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	28 ± 7.8	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	26 ± 5.7	2.4 ± 0.9	4.5 ± 1.7	18	2.7 ± 0.9	24 ± 8	94

n.d.: not detected

A-4-a Milled samples

Table A-24: Extracted portions from the aluminium samples R-AO-1, R-AO-2 and W-RS-1 and the uranium samples W-T-1, W-T-2 and W-T-3; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
R-AO-1, <0.1mm	^{238}U	130 ± 19	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	231 ± 17	43 ± 1.6	90 ± 3.3	39	1 ± 0.8	12 ± 7.1	5
	^{214}Pb	216 ± 15	43 ± 1.5	92 ± 3.2	42	1.3 ± 0.8	12 ± 7.1	5
	^{214}Bi	245 ± 19	42 ± 1.6	89 ± 3.4	37	1.5 ± 0.8	13 ± 7.1	6
	^{210}Pb	423 ± 38	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	176 ± 16	5 ± 0.9	11 ± 1.9	6	n.d.	-/-	-/-
	^{228}Th	156 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-
R-AO-2, <0.1mm	^{238}U	862 ± 72	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	2182 ± 159	392 ± 11	826 ± 22	38	4.8 ± 0.8	45 ± 7	2
	^{214}Pb	2000 ± 137	402 ± 11	847 ± 24	42	4.1 ± 0.8	38 ± 7.4	2
	^{214}Bi	2363 ± 180	382 ± 9.6	805 ± 20	34	5.5 ± 0.7	51 ± 6.5	2
	^{210}Pb	3928 ± 293	11 ± 6	23 ± 13	0.6	n.d.	-/-	-/-
	^{228}Ra	169 ± 17	4.5 ± 3	9.5 ± 6.3	5.6	n.d.	-/-	-/-
	^{228}Th	147 ± 13	n.d.	-/-	-/-	n.d.	-/-	-/-
W-RS-1, <0.1mm	^{238}U	191 ± 26	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	195 ± 15	6.2 ± 0.9	13 ± 1.9	7	6 ± 1.1	61 ± 9.9	31
	^{214}Pb	186 ± 13	6.3 ± 0.9	13 ± 1.9	7	5.8 ± 1	55 ± 9.5	30
	^{214}Bi	203 ± 16	6.1 ± 0.9	13 ± 1.9	6	7 ± 1.1	66 ± 10	33
	^{210}Pb	329 ± 39	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	516 ± 43	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	459 ± 36	n.d.	-/-	-/-	n.d.	-/-	-/-
W-T-1, <0.1mm	^{238}U	1553 ± 246	350 ± 29	681 ± 56	44	n.d.	-/-	-/-
	^{226}Ra	4691 ± 280	931 ± 24	1811 ± 47	39	4.8 ± 0.6	45 ± 5.4	1
	^{214}Pb	4571 ± 289	1010 ± 25	1965 ± 49	43	4.3 ± 0.5	41 ± 4.2	0.9
	^{214}Bi	4810 ± 271	852 ± 23	1658 ± 45	35	5.2 ± 0.7	49 ± 6.6	1
	^{210}Pb	9189 ± 748	21 ± 14	41 ± 27	0.4	n.d.	-/-	-/-
	^{228}Ra	31 ± 3.3	n.d.	-/-	-/-	2 ± 0.8	19 ± 7.5	60
	^{228}Th	32 ± 2.7	33 ± 1.8	64 ± 3.5	100	2.1 ± 0.9	20 ± 8.5	60
W-T-2, <0.1mm	^{238}U	1875 ± 297	n.d.	-/-	-/-	6.5 ± 2.1	61 ± 20	3
	^{226}Ra	5556 ± 332	1086 ± 28	2213 ± 57	40	2.3 ± 0.5	22 ± 4.7	0.4
	^{214}Pb	5433 ± 344	1171 ± 29	2387 ± 59	44	2.6 ± 0.4	24 ± 3.7	0.4
	^{214}Bi	5678 ± 320	1000 ± 27	2039 ± 55	36	2 ± 0.6	19 ± 5.6	0.3
	^{210}Pb	10,260 ± 833	52 ± 15	106 ± 30	1	n.d.	-/-	-/-
	^{228}Ra	29 ± 3.2	5.4 ± 1.9	11 ± 3.9	38	1.8 ± 0.8	17 ± 7.5	59
	^{228}Th	27 ± 2.4	3 ± 1.8	6.1 ± 3.7	22	1.8 ± 0.9	17 ± 8.4	62
W-T-3, <0.1mm	^{238}U	n.d.	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{226}Ra	9754 ± 583	205 ± 5.8	404 ± 11	4	7.3 ± 0.7	68 ± 6	0.7
	^{214}Pb	9601 ± 607	222 ± 5.9	438 ± 12	5	8 ± 0.6	74 ± 5.6	0.8
	^{214}Bi	9907 ± 558	187 ± 5.7	369 ± 11	4	6.6 ± 0.7	61 ± 6.5	0.6
	^{210}Pb	15,910 ± 1291	42 ± 8.7	83 ± 17	0.5	n.d.	-/-	-/-
	^{228}Ra	33 ± 4	n.d.	-/-	-/-	2 ± 0.7	19 ± 6,5	57
	^{228}Th	31 ± 3	2.7 ± 1.2	5.3 ± 2.4	17	2.7 ± 0.9	25 ± 8.4	81

n.d.: not detected

Table A-25: Extracted portions from the uranium samples W-T-4 and U-S-5 and U-S-6; given error quotes to 2σ-reliability.

sample		initial specific activity	DIN 19730			DIN 38414/S4		
		[Bq/kg]	[Bq/l]	[Bq/kg]	[%]	[Bq/l]	[Bq/kg]	[%]
W-T-4, <0.1mm	^{238}U	1773 ± 280	119 ± 12	238 ± 23	13	n.d.	-/-	-/-
	^{226}Ra	3011 ± 180	409 ± 11	818 ± 22	27	1 ± 0.3	7 ± 2.8	0.1
	^{214}Pb	2955 ± 187	446 ± 12	892 ± 23	30	0.6 ± 0.3	5.6 ± 2.8	0.2
	^{214}Bi	3066 ± 173	372 ± 11	744 ± 21	24	0.8 ± 0.3	7.5 ± 2.8	0.2
	^{210}Pb	7844 ± 639	20 ± 8.6	40 ± 17	0.5	n.d.	-/-	-/-
	^{228}Ra	28 ± 2.5	n.d.	-/-	-/-	2.2 ± 1	21 ± 9.4	74
	^{228}Th	30 ± 2.1	2.1 ± 1.5	4.2 ± 3	14	1.8 ± 0.9	17 ± 8.4	57
U-S-5, <0.1mm	^{238}U	64 ± 15	n.d.	-/-	-/-	4.2 ± 3.5	38 ± 32	60
	^{226}Ra	60 ± 5	2.6 ± 0.6	4.8 ± 1.1	8	n.d.	-/-	-/-
	^{214}Pb	55 ± 4.2	2.2 ± 0.4	4.2 ± 0.8	8	n.d.	-/-	-/-
	^{214}Bi	64 ± 5.7	2.9 ± 0.8	5.5 ± 1.5	9	n.d.	-/-	-/-
	^{210}Pb	66 ± 20	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	11 ± 7	1.6 ± 1.7	3 ± 2.7	28	n.d.	-/-	-/-
	^{228}Th	13 ± 1.6	3 ± 1	5.7 ± 1.9	15	2.4 ± 0.9	22 ± 8.2	56
U-S-6, <0.1mm	^{238}U	842 ± 74	23 ± 5.1	43 ± 9.8	5	n.d.	-/-	-/-
	^{226}Ra	830 ± 61	5.3 ± 0.7	10 ± 1.3	1	n.d.	-/-	-/-
	^{214}Pb	765 ± 53	5.8 ± 0.6	11 ± 1.2	2	n.d.	-/-	-/-
	^{214}Bi	894 ± 68	4.8 ± 0.8	9.2 ± 1.5	1	n.d.	-/-	-/-
	^{210}Pb	764 ± 68	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Ra	28 ± 7.8	n.d.	-/-	-/-	n.d.	-/-	-/-
	^{228}Th	26 ± 5.7	3 ± 0.9	5.8 ± 1.7	23	2.1 ± 0.9	18 ± 7.8	72

n.d.: not detected

A-5 Radon emanation rates

Table A-26: Radon emanation rates of all the solid TENORM samples.

sample		weight [g]	$counts_{netto}$	^{222}Rn concentration [Bq/l]	^{222}Rn emanation [Bq/kg]
phosphate industry	R-PO-1, <2mm	174	2708	2.22	21.7 ± 1.5
	R-PO-2, <2mm	222	34	0.03	0.2 ± 0.02
	W-PG-1, <2mm	120	48	0.04	0.6 ± 0.04
	P-F-1, <2mm	144	955	0.78	9.3 ± 0.6
	P-F-2, <2mm	179	977	0.8	7.7 ± 0.5
aluminium industry	R-AO-1, <2mm	143	1148	0.95	11.3 ± 0.79
	R-AO-1, <0.1mm	117	932	0.89	12.96 ± 0.91
	R-AO-2, <2mm	146	21,735	18	210.2 ± 14.7
	R-AO-2, <0.1mm	100	9017	8.6	147.5 ± 10.3
	W-RS-1, <2mm	83	222	0.18	3.74 ± 0.26
	W-RS-1, <0.1mm	112	163	0.16	2.39 ± 0.17
refractory industry	R-ZS-1, <2mm	297	465	0.42	2.44 ± 0.17
	R-ZS-1, <0.1mm	244	875	0.72	5 ± 0.35
	W-FD-1, <0.1mm	28	7	0.01	0.39 ± 0.03
	P-FZM-1, <2mm	197	2	0.002	0.02 ± 0.001
	P-FZM-1, <0.1mm	200	130	0.11	0.9 ± 0.06
	P-FZM-2, <0.1mm	97	207	0.19	3.36 ± 0.23
crude oil exploitation	W-SL-1, <2mm	118	10,158	8.3	120 ± 8.4
	W-SL-2, <2mm	87	29,048	29.2	571 ± 40
	W-SC-1, <2mm	167	4663	4.7	48.1 ± 3.37
	W-SC-2,<2mm	143	2650	2.68	32 ± 2.24
uranium industry	R-UO-1, <0.1mm	175	29,928	244.6	2385 ± 167
	W-T-1, <2mm	139	11,240	9.23	113.2 ± 7.9
	W-T-2, <2mm	167	9937	8.17	83.8 ± 5.9
	W-T-3, <2mm	144	20,377	16.8	200 ± 14
	W-T-4, <2mm	172	4699	3.88	38.5 ± 2.7
	U-ST-1, <0.1mm	249	59	0.05	0.33 ± 0.02
	U-ST-2, <0.1mm	264	21	0.02	0.11 ± 0.01
	U-ST-3, <0.1mm	186	4069	3.32	30.6 ± 2.1
	U-ST-4, <0.1mm	233	3750	3.06	22.5 ± 1.6
	U-S-5, <2mm	97.7	150	0.12	2.14 ± 0.15
	U-S-6, <2mm	79.6	1663	1.36	29.2 ± 2.05

LEBENSLAUF

PERSÖNLICHE DATEN

Name:	Karsten Leopold
geboren:	11. Februar 1975
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Familienstand:	ledig

SCHULBILDUNG

1981 - 1985	Städt. Grundschule Meyerstraße, Wuppertal-Heckinghausen
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ZIVILDIENST

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13.10.1995 - 23.11.2001	Studium der Geologie/Paläontologie an der Westfälischen Wilhelms-Universität Münster
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- Karsten Leopold -

Erklärung:

Hiermit erkläre ich gemäß § 6 Abs. 2 Nr. 7 der weiterhin geltenden Promotionsordnung der Fachbereiche 6 bis 9 zur Erlangung des Dr. rer. nat., dass ich das Arbeitsgebiet, dem das Thema „Chemical types of bounding of natural radionuclides in TENORM (*Technologically Enhanced Naturally Occurring Radioactive Materials*)" zuzuordnen ist, in Forschung und Lehre vertrete und den Antrag von Herrn Karsten Leopold befürworte.

Essen, den 24.05.2007

- PD Dr. Jens Wiegand -

Erklärung:

Hiermit erkläre ich gemäß § 6 Abs. 2 Nr. 6 der weiterhin geltenden Promotionsordnung der Fachbereiche 6 bis 9 zur Erlangung des Dr. rer. nat., dass ich die vorliegende Dissertation selbstständig verfasst und mich keiner anderen als der angegebenen Hilfsmittel bedient habe.

Essen, den 24.05.2007

- Karsten Leopold -

Erklärung:

Hiermit erkläre ich gemäß § 6 Abs. 2 Nr. 8 der weiterhin geltenden Promotionsordnung der Fachbereiche 6 bis 9 zur Erlangung des Dr. rer. nat., dass ich keine anderen Promotionen bzw. Promotionsversuche in der Vergangenheit durchgeführt habe und dass diese Arbeit von keiner anderen Fakultät abgelehnt worden ist.

Essen, den 24.05.2007

- Karsten Leopold -